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EFFLUENT SEPARATION BY SURFACE-
ACTIVE AGENTS

Robert E. Baier, et al

Calspan Corporation

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20. ABSTRACT (contd.)

experiments involved mixing the agglomerates to be separated with various solid spreading aids, liquid spreading aids, adhesive and autophobic agents. Agglomerates treated with such materials were then exposed to interfacial stresses expected to supply the energy necessary to array these mixtures into monolayer surface films. Of the many experimental methods investigated, the best technique found to achieve particle deagglomeration is based upon surface chemical methods of generating stable colloidal suspensions. In its simplest form, the selected separation method involves a first step ultrasonic dispersion of particulate material in the presence of one of the spreading aids listed above. This stable colloidal dispersion of separated particles is then carefully introduced to a gas/liquid interface in order to transform the particles in the volume phase into a permanent two-dimensional array. Polymeric spreading aids serve the purpose of distributing the particles over the surface and fixing them in an immobile binder layer. Results obtained using this technique indicate that most natural agglomerates and conglomerates can be effectively broken down into their individual component particles.

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EFFLUENT SEPARATION BY SURFACE-ACTIVE AGENTS

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Prepared For:

AIR FORCE TECHNICAL APPLICATIONS CENTER
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FOREWORD

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The authors appreciate technical contributions made during the performance of this program by Calspan personnel Paul Schnizler, Teresa Amabile, Dr. Michael Terlecky, Dennis Goupil, Shirley Perlmutter, William Hancock, and Dr. Ulrich Katz. Manageral contributions were made by D.B. Dahm and R.J. Pilie'.

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Section 1

SUMMARY

The purpose of this program was to apply basic surface chemical theory to developing simple means for nondestructively separating the submicrometer constituents of complex multicomponent agglomerates obtained as samples for environmental quality assessment. The techniques evaluated in this program do not significantly modify the constituents while arraying them on substrates suitable for microscopic, spectroscopic, or x-ray analysis. Typical experiments involved mixing the agglomerates to be separated with various solid spreading aids, liquid spreading aids, adhesive and autophobic agents. Agglomerates treated with such materials were then exposed to interfacial stresses expected to supply the energy necessary to array these mixtures into monolayer surface films.

Of the many experimental methods investigated, the best technique found to achieve particle deagglomeration is based upon truly classical surface chemical methods of generating stable colloidal suspensions. In its simplest form, the selected separation method involves as a first step ultrasonic dispersion of particulate material in the presence of one of the spreading aids listed above. This stable colloidal dispersion of separated particles is then carefully introduced to a gas/liquid interface in order to transform the particles in the volume phase into a permanent two-dimensional array. Polymeric spreading aids serve the purpose of distributing the particles over the surface and fixing them in an immobile binder layer. Results obtained using this technique indicate that most natural agglomerates and conglomerates can be effectively broken down into their individual component particles.

Figure 1 schematically illustrates the group of surface chemistry approaches evaluated in this project. Although all of the approaches outlined in Figure 1 were used, we discuss only the major experimental concepts and results in this report (Section 3). Even better and more efficient particle separations should be possible with directed extensions of the research just completed. Brief recommendations for future work are outlined in Section 5.

PROJECT ESSAA EFFLUENT SEPARATION BY SURFACE ACTIVE AGENTS EXPERIMENTAL APPROACHES

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NOTE: TO EFFECTUALLY SEPARATE THE PARTICLES, IT IS NECESSARY TO OBTAIN THE USE OF COMPLETELY WETTABLE PARTICLES. ALL PARTICLES MUST BE COMPLETELY WETTABLE. PARTICLES THAT ARE NOT COMPLETELY WETTABLE WILL NOT BE SEPARATED. PARTICLES THAT ARE NOT COMPLETELY WETTABLE WILL NOT BE SEPARATED. PARTICLES THAT ARE NOT COMPLETELY WETTABLE WILL NOT BE SEPARATED.

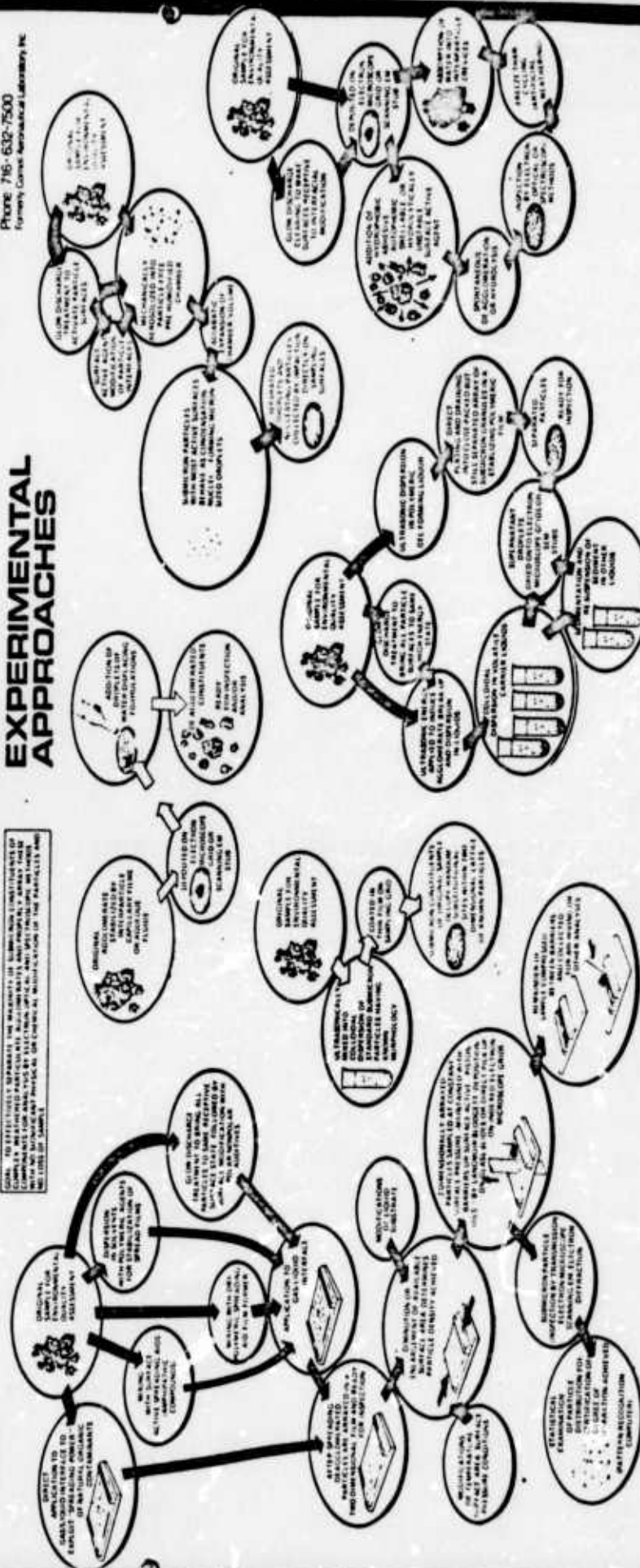


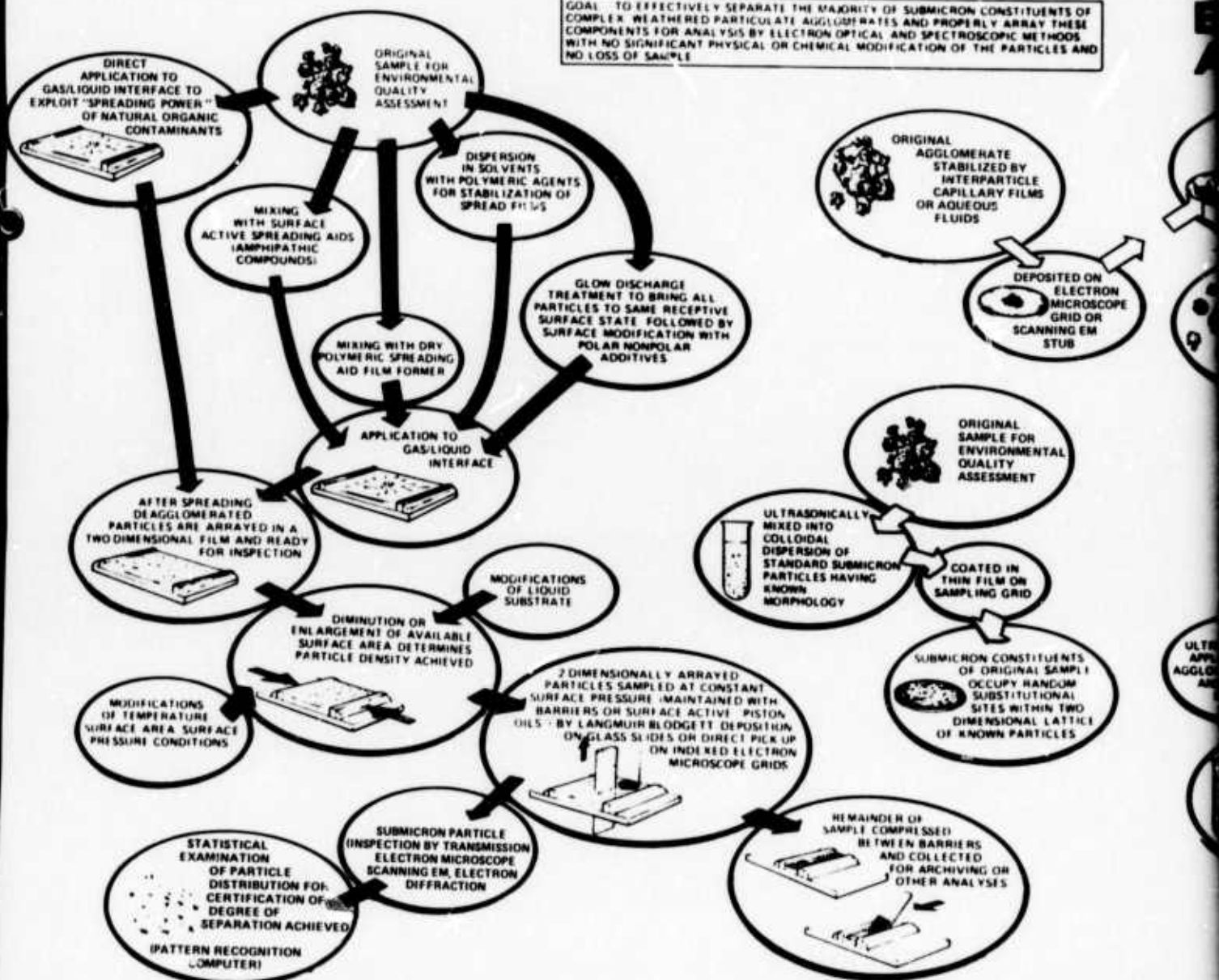
Figure 1 EFFLUENT SEPARATION BY SURFACE ACTIVE AGENTS APPROACHES

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R.E. BAIER

PROJECT ENGINEER
V.A. DEPALMA

PROJECT E EFFLUENT SEPARATION BY S

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JECT ESSAA N BY SURFACE ACTIVE AGENTS

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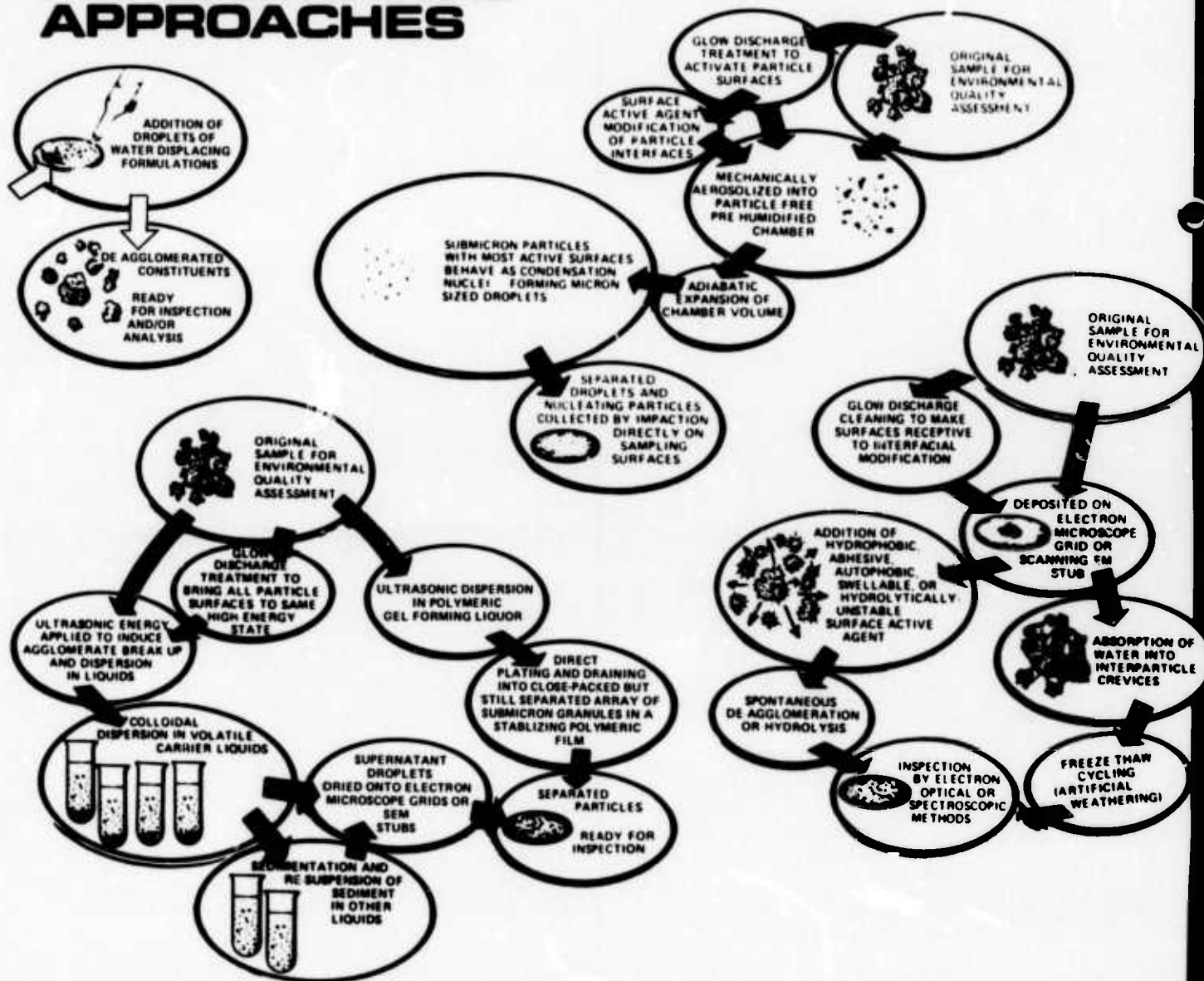


Figure 1 EFFLUENT SEPARATION BY SURFACE-ACTIVE AGENTS APPROACHES

Section 2
INTRODUCTION

Calspan Corporation, under the sponsorship of the Air Force Technical Applications Center, Patrick Air Force Base, Florida has conducted an investigation into the potential improvements in deagglomeration of particulate materials by the use of surface-active agents. The techniques developed in this program have proven equally useful with artificially and naturally weathered materials.

This final report summarizes results of technical work performed over the period of February 1972 through October 1973. Monthly and quarterly reports issued in the interim reviewed details of the various project activities during each phase of the program. In this report, the various experimental techniques used to effect particle deagglomeration are only briefly discussed under their typical categories. The end of each section contains a summary of the application of each technique along with recommendations for its use. The best experimentally developed technique is then described as applied to weathered samples. Brief recommendations for future work are given in the last section of the report.

Section 3

TECHNICAL DISCUSSION

In this program, surface chemical and physical methods were applied to the problem of developing techniques to nondestructively separate the sub-micron constituents of complex agglomerates. Six groups of techniques (shown in Figure 1) were investigated. These are:

- Gas/liquid interfacial spreading
- Use of intrinsic wetting properties
- Use of hydrophobic, adhesive or unstable wetting agents
- Substitutional replacements
- Reduction of particle surface-energy state
- Separation by nucleation

Each group is discussed separately in a subsequent subsection. Techniques investigated in addition to the six basic groups are treated in Subsection 3.7.

3.1 PARTICLE DEAGGLOMERATION BY GAS/LIQUID INTERFACIAL SPREADING

Gas/liquid interfacial forces were originally selected as the primary candidate method of producing particle separation because of our previous successful experience in the formation of a large variety of monomolecular surface films.

This technique for separating agglomerated particles requires any naturally acquired or deliberately applied organic coating on the agglomerated particles to be sufficient to force the particles apart when they are introduced to the gas/liquid interface. The organic coatings can be derived from predetermined treatments or result from environmental weathering.

An estimate of the forces operating at the air/water interface is easily deduced. For example, as a polymer spontaneously spreads on water to a monolayer thickness of less than 30 Å, it can generate a surface pressure (or surface tension depression) equal to 30 dynes/cm. Within the volume of the spread film, this can be recalculated as representing a negative pressure of the order of 100 atmospheres in the plane of the film. If the particles to be deagglomerated were coated with such a film-forming agent, they should theoretically be well separated when dragged along the surface with the spreading polymer. During this interfacial study, it was not possible to routinely achieve the required isotropic spreading forces at the air/liquid interface to produce uniform large-scale particle deagglomeration without preliminary (e.g., ultrasonic) dispersion of the samples.

The various interfacial spreading techniques investigated and the Subsections in which they are discussed are:

- Sprinkling on suitable substrate (control group for comparison with other techniques) - 3.1.1.
- Direct application to the air/liquid interface - 3.1.2.
- Mixing with low molecular weight surface-active spreading aids-3.1.3.
- Mixing with dry spreading aids and film formers-3.1.4.
- Dispersion in wetting agents with polymeric agents added for spreading and stabilization - 3.1.5.
- Ultrasonic treatment in liquid spreading aids-3.1.6.

These separation techniques employing interfacial forces are schematically reviewed in Figure 1. Section 3.1.7 summarizes the results of using these techniques.

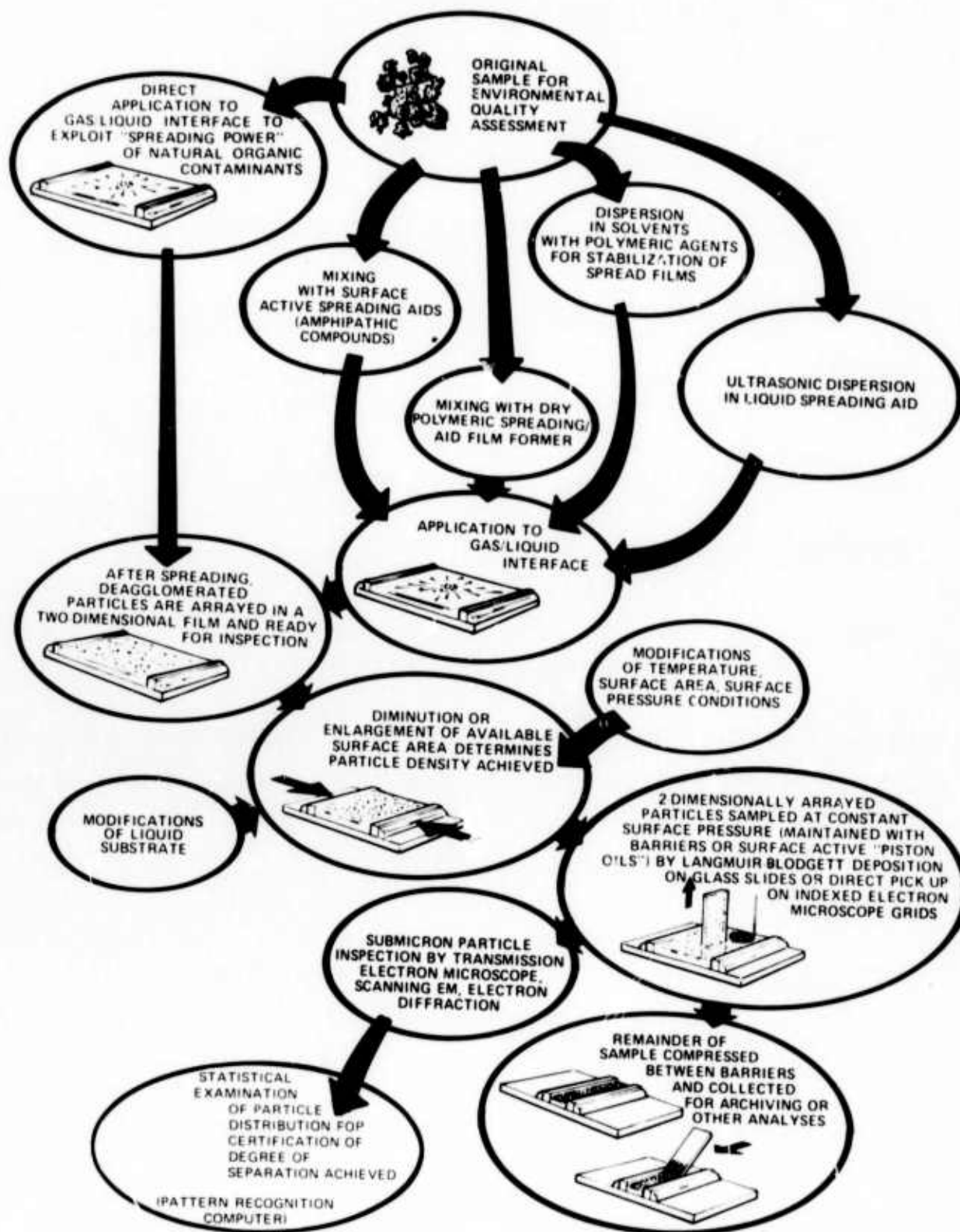


Figure 2 PARTICLE DEAGGLOMERATION BY GAS/LIQUID INTERFACE SPREADING

3.1.1 Separation by Sprinkling on a Suitable Substrate

Some degree of particle deagglomeration has been achieved simply by application of as-received particle agglomerates to the air/water interface. When this result is compared to results obtained by simply sprinkling particles on a prepared transmission electron microscope grid (TEM), it is clear that some particle deagglomeration has occurred. To initially characterize the particles in terms of their as-received condition, they were sprinkled on a suitable substrate and typical areas of particles photographed. Photographs are presented for the following particles: clay; carbon (Aqua Nuchar); glass microbeads; Apollo 15 moon dust, and calibrating carbon. These photographs (Figures 3 - 7) allow comparison with photographs to be presented later.

A relative assessment of the particle separation obtained by the different techniques used in this project was best obtained by visual inspection of electron micrographs of each particular sample.

Clay - Figure 3 shows the particle distributions produced by simple sprinkling of clay particles. The shadows in these figures were made by germanium-shadowing the grids prior to examination in a transmission electron microscope (TEM). The absence of clay particles for many of the shadows shown, indicates that they were lost in the viewing process. This was substantiated by observations made while examining the particles in the TEM.

Carbon (Aqua Nuchar) - Figure 4 is typical of the particle display for Aqua-Nuchar carbon prepared by simple sprinkling.

Glass Microbeads - Figure 5 shows two typical areas for glass microbeads sprinkled on a TEM grid. The initial degree of particle separation shown is very low. Many of the larger particles are lost in the viewing process.

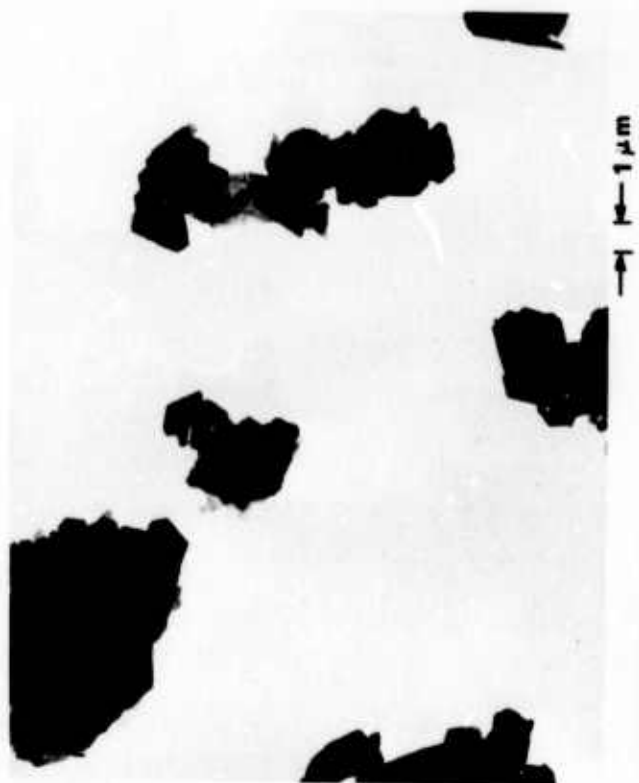
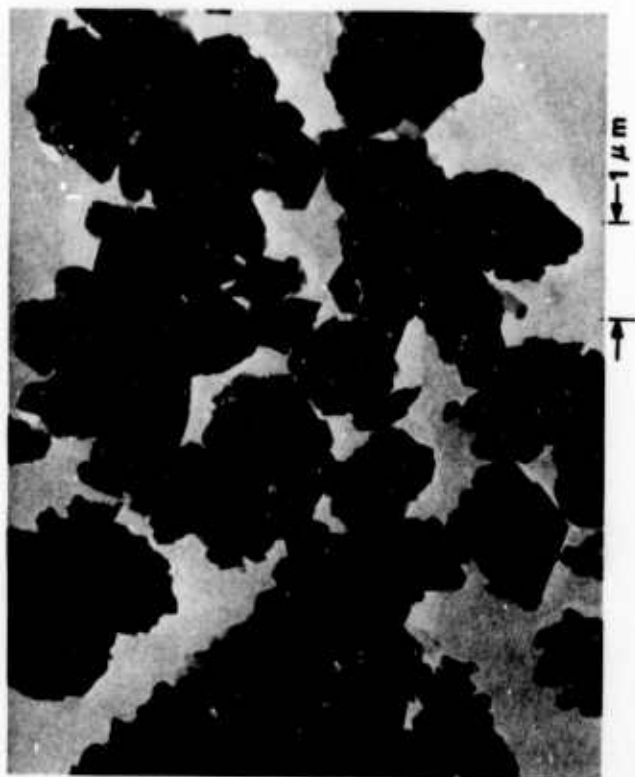
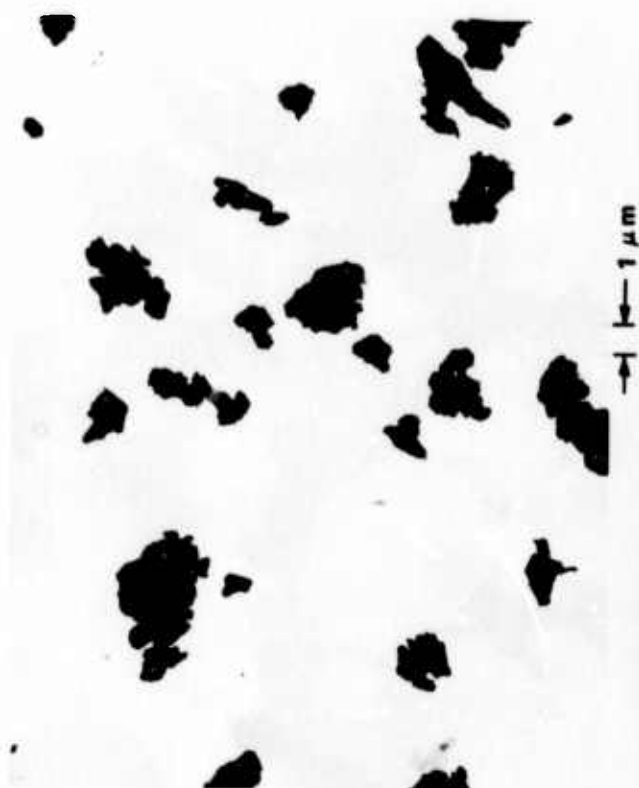


Figure 3 CLAY SPRINKLED ON A PREPARED TEM GRID

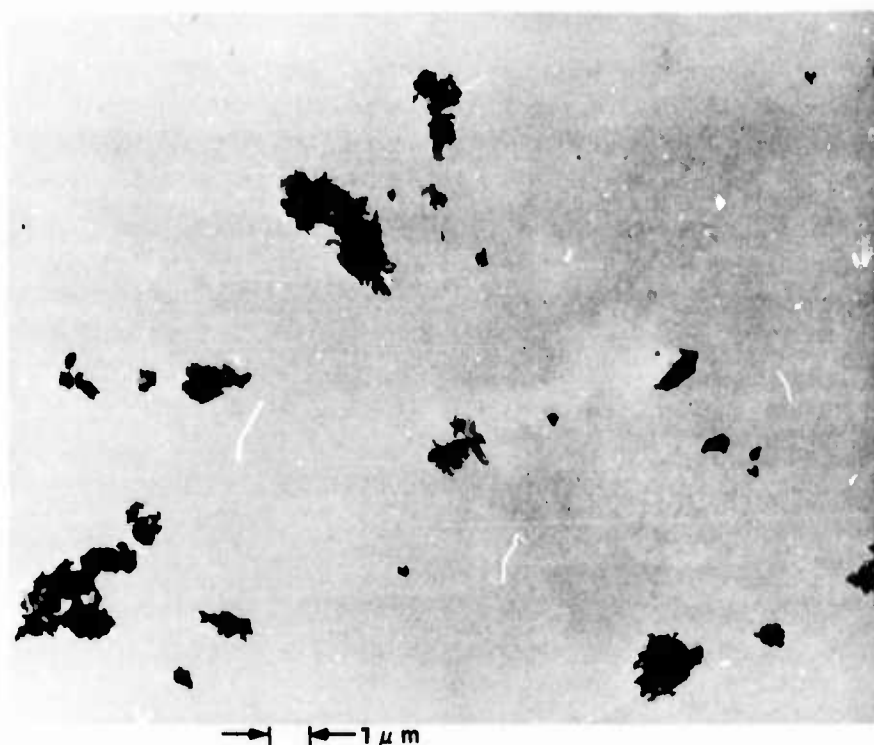


Figure 4 AQUA-NUCHAR CARBON PARTICLES PREPARED BY SPRINKLING ON A PREPARED TEM GRID

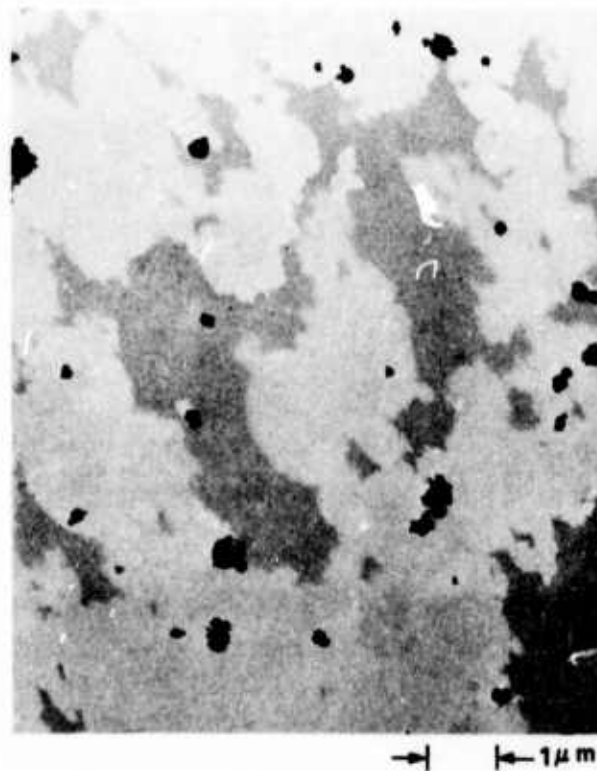
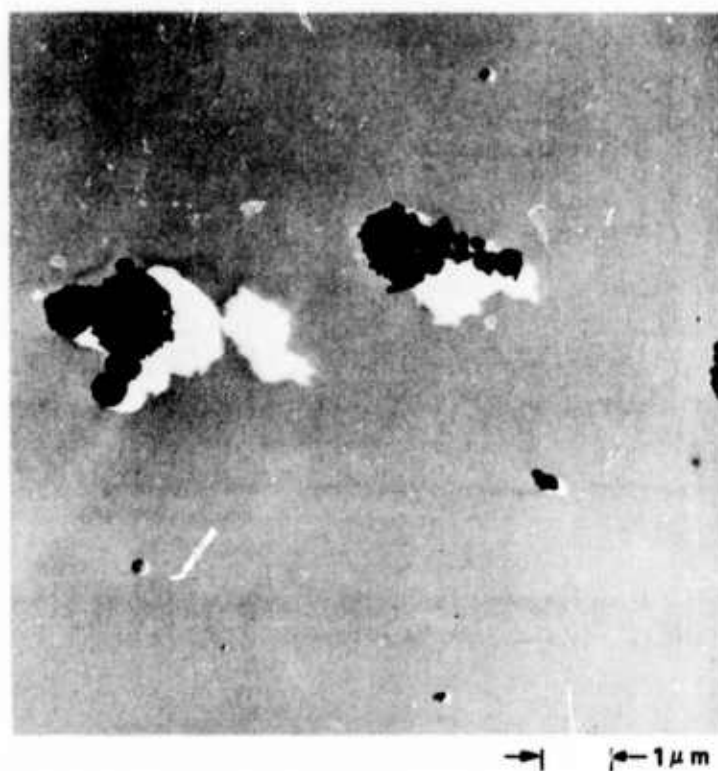


Figure 5 TYPICAL AREAS OF GLASS MICROBEADS SPRINKLED ON A PREPARED TEM GRID

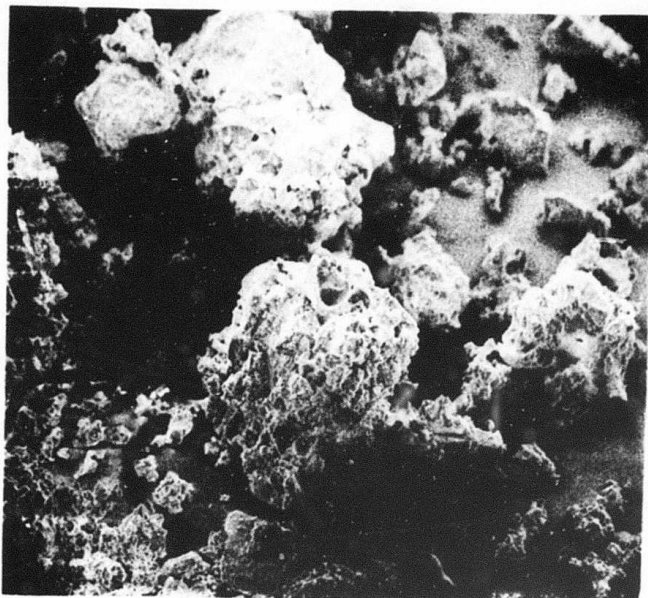
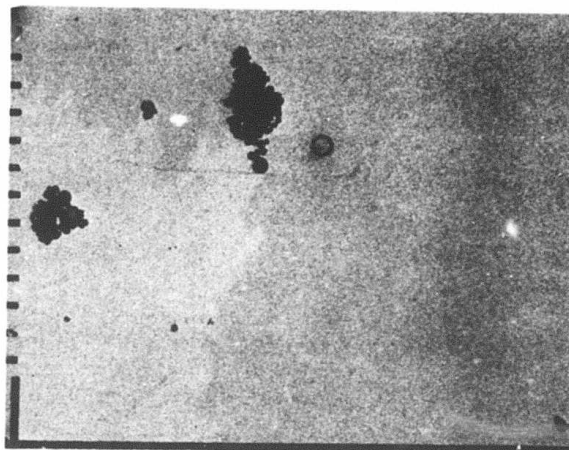
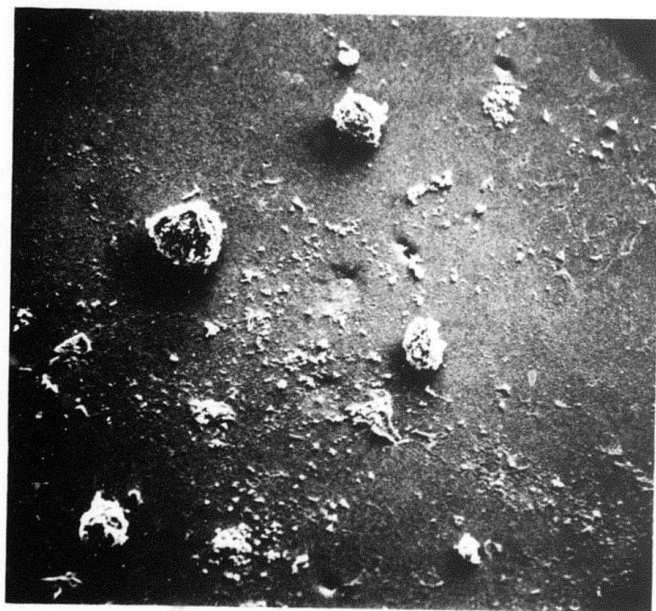


Figure 6 APOLLO 15 MOON DUST SPRINKLED ON SEM STUB



7(b) TEM GRID



7(a) SEM STUB

Figure 7 CALIBRATING CARBON SPRINKLED ON A SEM STUB AND TEM GRID

Apollo #15 Moon Dust - Moon dust from Apollo 15 was examined in its as-received condition by sprinkling on a scanning electron microscope (SEM) stub covered with double-coated adhesive tape. Figure 6 shows a SEM photo of a typical particle dispersion produced in this way.

Calibrating Carbon - Calibrating carbon, because of its inertness and high degree of uniform sized particles was chosen as the primary material with which to evaluate most of the proposed particle deagglomeration techniques. This material, as supplied, is highly agglomerated. However, very little energy is needed to break apart an agglomerated particle into its component individual spherical particles. Figure 7 shows calibrating carbon sprinkled on a SEM stub (in a) and a TEM grid (in b). Agglomerates (20 μm dia.) are present in large numbers in the sprinkled sample. These large agglomerates do not remain adherent to the TEM grid; consequently only their shadow is visible in Figure 7b.

On occasion, individual particles are detected in particle preparations resulting from sprinkling the as-received material. These single particles are present in such a small number, however, that any increase in their number is indicative of particle deagglomeration. For example, as indicated in a magnified view of an agglomerate of moon dust (Figure 8), it is the intent of a particle deagglomeration technique to remove and display singly those submicron particles shown which are attached to the larger central mass. We have not found it possible to routinely effect intrinsic separations of such particles so that a given submicron particle in Figure 8 could be extracted for examination.

3.1.2 Direct Application of Agglomerated Particles to Air/Liquid Interfaces

This subsection documents results of particle separation attempts made with as-received particles introduced directly to the air/water interface. No organic additives or spreading aids were used in this technique. Spreading of natural organic contaminants on the particles was mainly responsible for the observed particle separations. Visual observations made for the material placed

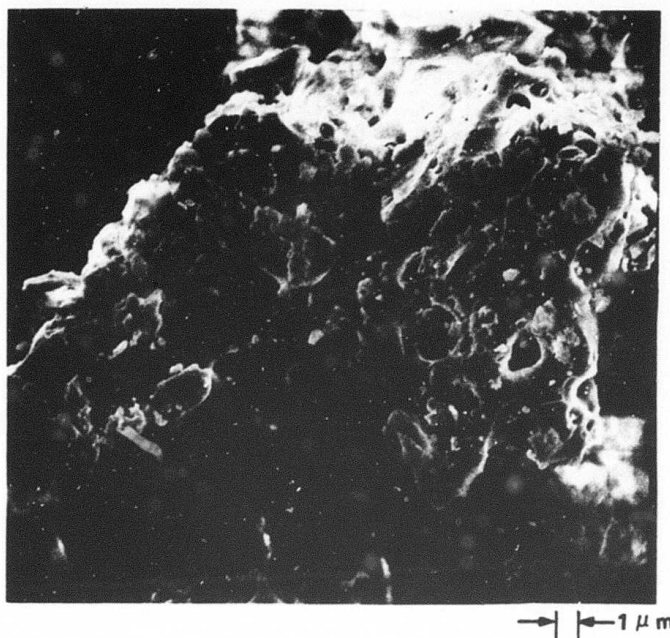


Figure 8 APOLLO 15 MOON DUST SHOWING ATTACHED PARTICULATES

on the water surface were just as important as the electron microscopic views of particles retrieved from the liquid surface in judging the success or failure of these experiments.

The procedure described in this section is typical of all work involving spreading at gas/liquid interfaces. Appendix 2 describes the automated surface balance used in these experiments. The trough in this apparatus is completely Teflon-lined, making it inert and easy to cleanse of organic contaminants. Hydraulic lift devices shown in the figure in Appendix 2 are used to retrieve surface samples by raising prepared TEM grids up through the liquid surface. The material to be deagglomerated was usually sprinkled onto an air/water interface using the wood end of a cotton-tipped applicator. Prior to this, the water surface was swept several times with a Teflon rod to remove any surface contaminants from the water. This step is extremely important because

traces of organic materials on the water surface usually prevent the desired degree of particle spreading. The following materials have been investigated for their potential deagglomeration as achieved by simply applying them to an air/water interface: clay; carbon (Aqua Nuchar); glass microbeads; Apollo 15 moon dust, and calibrating carbon.

Clay - Samples of as-received clay sprinkled on the air/water interface and allowed to equilibrate for 15 minutes were retrieved on prepared TEM grids by using the hydraulic lifts in the Langmuir trough. Figure 9 shows typical views of clay particles prepared in this way. Comparison of these photos with Figure 3 indicates that little deagglomeration was achieved.

Carbon (Aqua Nuchar) - When sprinkled on water, this material initially has the same appearance as when sprinkled on a solid surface. Within several minutes large clumps of particles on the water surface begin to break down into a multilayer carbon carpet. However, no true particle deagglomeration occurs. When a prepared TEM grid is raised through the water surface, disruptive forces are set up which further break down the spread carbon. Figure 10 shows typical views of carbon prepared in this way. Because of the high surface area of this material, it is expected that forces brought about by capillary penetration through the large clumps are partially responsible for agglomerate breakdown.

Glass Microbeads - When glass microbeads are introduced to the water surface, many of the dense, large clumps of particles sink. Particle spreading takes place only during the short time it takes for the particle clumps to break through the air/water interface. Prepared TEM grids lifted through the surface entrain very few particles. Figure 11 shows the particle arrays present on the water as a result of this technique. The glass microbeads have not been deagglomerated as a result of this treatment as confirmed by comparison with typical areas in Figure 5. Visual observation during drying, using light microscopy, showed redistribution of the particles picked up on the prepared grid as a result of evaporation of the residual water. Observation of such redistribution made it highly improbable, then, that simple spreading

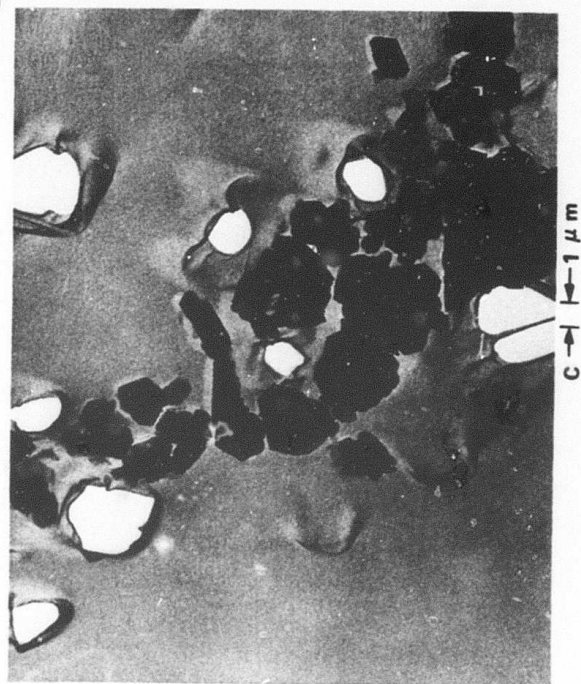
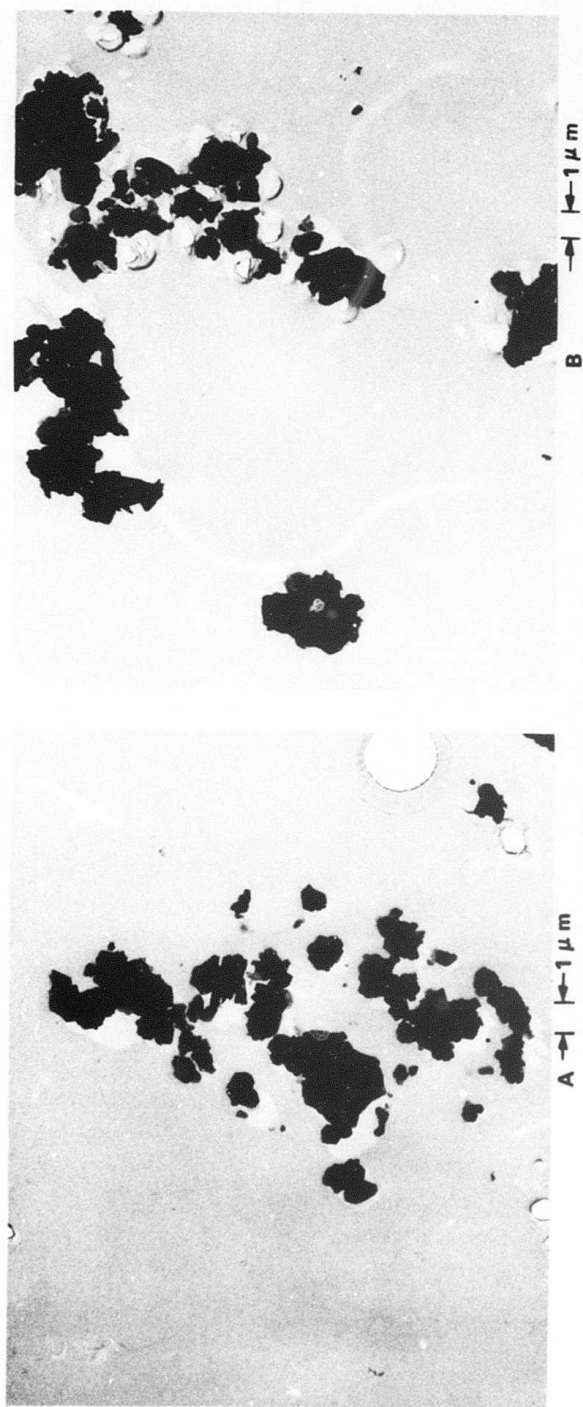


Figure 9 CLAY PARTICLES SPRINKLED ON WATER AND PICKED UP ON A PREPARED TEM GRID

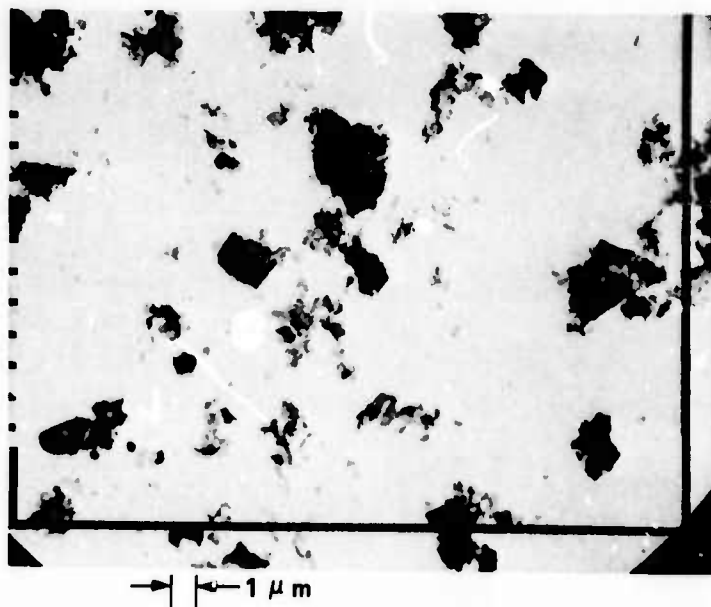
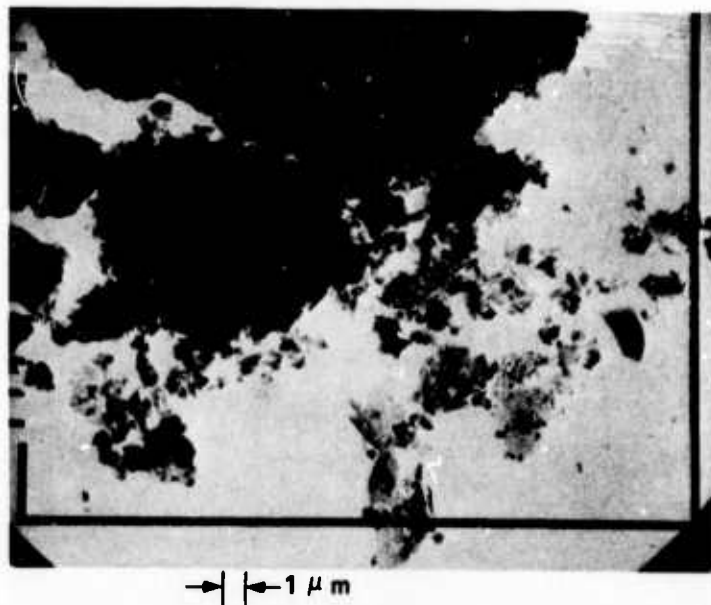
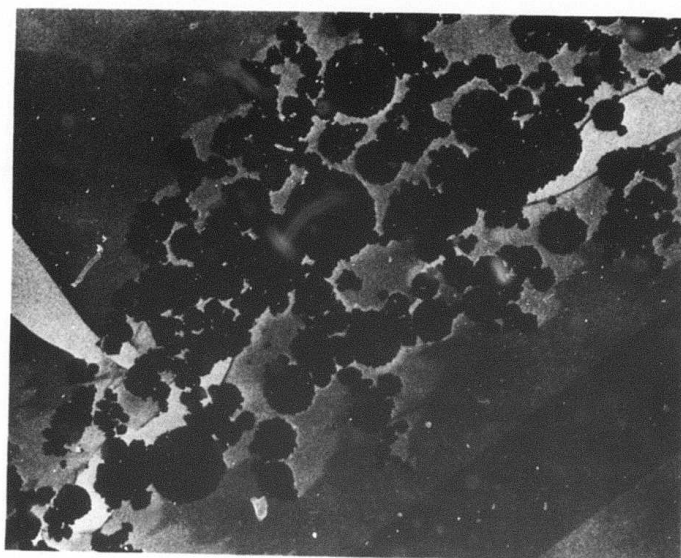
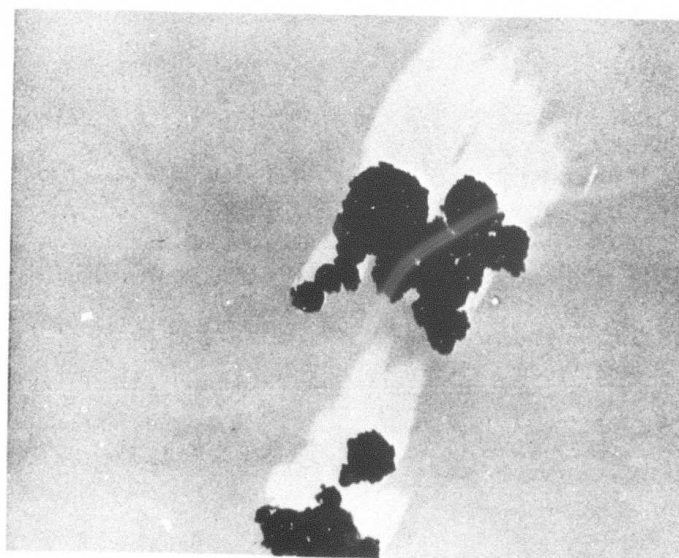


Figure 10 CARBON-AQUA NUCHAR SPRINKLED ON WATER



→ | ← 1 μm



→ | ← 1 μm

Figure 11 GLASS MICROBEADS SPRINKLED ON WATER AND PICKED UP ON PREPARED TEM GRID

of material on water, even if it did produce particle deagglomeration, could be of use in the absence of a stabilizing layer. As described later, support films formed at the surface along with the particles did rigidly hold the particles in place as desired.

Apollo 15 Moon Dust - Most of this material does not sink when sprinkled on a clean water surface; neither does it deagglomerate. This is indicated by the large number of agglomerates shown in Figure 12 for a sample retrieved from the water surface. This SEM view demonstrates that any redistribution of particles which took place upon evaporation of the water formed particle clumps mainly restricted to the copper grid surface of the TEM grid.

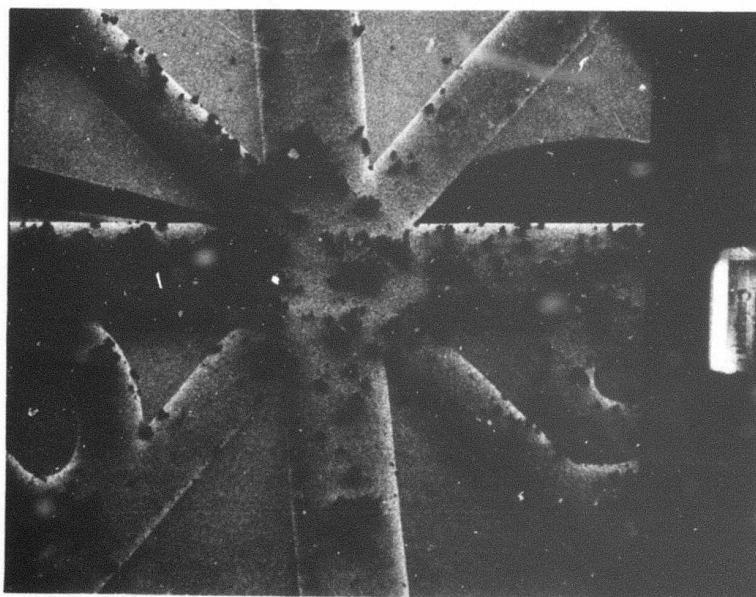


Figure 12 APOLLO 15 PARTICLES SPRINKLED ON WATER AND RETRIEVED ON A PREPARED TEM GRID

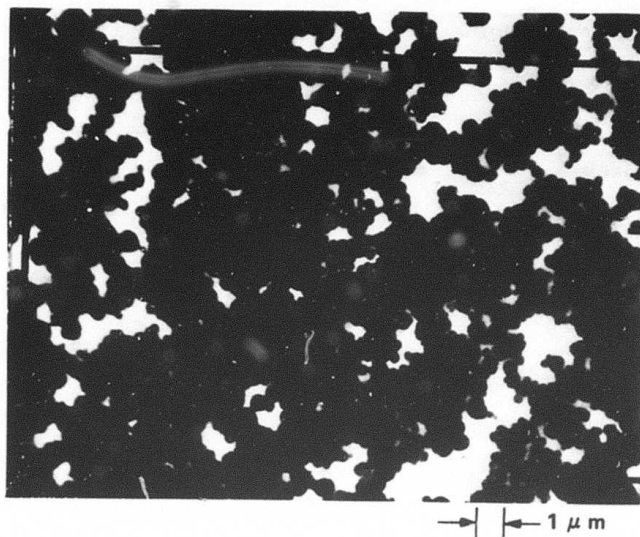
Calibrating Carbon - This material is not prone to sinking when applied to air/water interfaces; however, it does not routinely spontaneously separate. Figure 13a shows typical particle areas on a prepared TEM grid lifted through the water's surface. On occasion, areas such as in Figure 13b are seen; however, this separation is not solely a result of initial particle/air/water interface forces. More likely, it results when the particles are finally retrieved from the water's surface. In this sample, there is a noticeable improvement in the number of individual particles compared to the unspread case of Figure 7.

Thus, simple application of as-received, unweathered particles to the air/water interface will not produce the desired deagglomeration. Many particles do indeed deagglomerate but cannot be observed in this condition because they are redistributed and reagglomerated when they are retrieved and desiccated from the water surface. In most cases, the spreading forces are not sufficient to accomplish this goal in the absence of added organic spreading aids or adventitious organic contaminants.

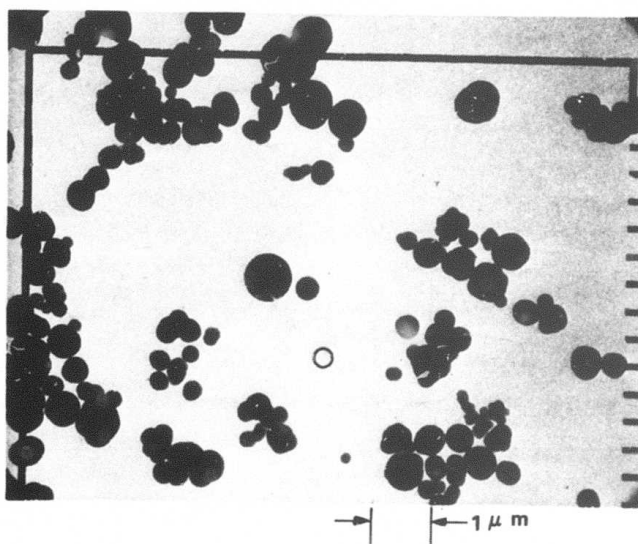
3.1.3 Particles Mixed with Low Molecular Weight Surface-Active Spreading Agents

To conserve limited funds and make maximum use of experimental resources, a choice had to be made as to which particulate material would be best for evaluation of the many separation techniques to be employed that relied on surface-active additives. Because of its inertness and uniform particle size, calibrating carbon was chosen. In this extensive series of experiments, the particles were admixed with at least one of the following agents:

1. Tertiary-Amyl alcohol
2. Benzene
3. Chloroform
4. Oleyl Alcohol
5. Oleic Acid



A



B

Figure 13 AS-RECEIVED CALIBRATING CARBON SPRINKLED ON WATER AND PICKED UP ON PREPARED TEM GRID

6. Sorbitan Trioleate
7. Isoamyl Alcohol
8. Butanol

The experiments done with each one of these spreading aids involved gently mixing calibrating carbon with the spreading aid and then introducing this mixture to the air/water interface. Several techniques were used to spread the mixture onto the water surface. These included spreading from a prewetted glass ramp that was inclined to the edge of the Langmuir trough, spreading from a silver disk (placed on the hydraulic lift) gently lowered into the water surface, and simple pipetting of a small quantity onto the water surface.

Sampling of the spread particles was done by raising prepared TEM grids through the surface or by touching the carbon coated side of prepared TEM grids to the water surface. In most cases, very low particle concentrations were observed, with many of the agglomerated particles remaining unspread from the glass ramp or the silver disk. When particles were pipetted onto the surface, they sometimes sank beneath the surface. After considerable effort to improve this situation, it was concluded that simple mixing of the particles with a spreading aid was insufficient to enhance particle deagglomeration at gas/liquid interfaces.

3.1.4 Particles Mixed with Dry Spreading Aids and Film Formers

Dry (usually polymeric) spreading aids were chosen from materials which, when introduced to the air/water surface, spontaneously spread to form a stable water-insoluble film. Gelatin for example, will spread to form a water insoluble film even though gelatin is inherently water soluble. A rigid film in which the particles are embedded was also beneficial as it prevented the redistribution of the spread particles from taking place when they were retrieved from the water surface.

Calibrating carbon was mixed with at least one of the following dry surface-active materials listed below. From previous experiments, it was known that each of these materials would form a tough, transparent film on the water surface.

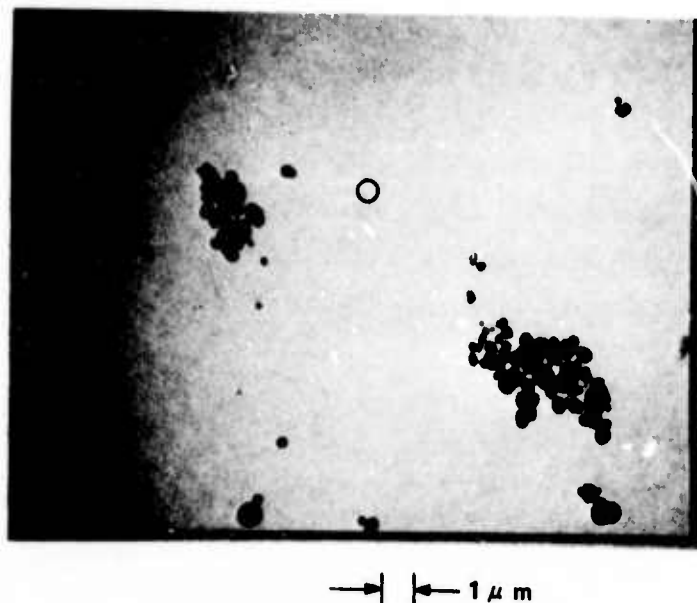
- Stearic Acid
- Cytochrome c
- Bovine Serum Albumin
- Acetyl Cholinesterase
- Octadecylamine

Some of these materials do not form a film capable of sustaining a high surface pressure; however, these were investigated because of their relative differences in surface activity. The technique in using these materials was to mix a few dry flakes of the material with a few milligrams of calibrating carbon. In the mechanical mixing process, the flakes became coated with carbon agglomerates. When these treated flakes were introduced to the air/water interface they spread spontaneously and upon doing so carried the carbon particles with the expanding film.

Observations made on prepared TEM grids raised through the water surface are typified by Figure 14 for calibrating carbon mixed with acetyl cholinesterase. This material behaved best in terms of producing a stable film. Also, this material spreads "explosively" when introduced to the air/water interface to form a tough interfacial film in which the particles are embedded.

The particle separation of Figure 14 was typical over the entire surface area; however, it did not routinely yield single carbon particles. The concentration of particles on the grid was readily increased by reducing the surface area over which the film was spread, either before or after film formation. This is easily done in the Langmuir trough.

As the results with this dry protein spreading aid were the best achieved, the method was also used with the particulate materials sent by the Air Force Technical Application Center. Even in the absence of spreading aids, UO_2 (ORNL) particles were observed to spontaneously spread on the water's



**Figure 14 CALIBRATING CARBON PARTICLES SPREAD ON WATER
USING ACETYL CHOLINESTERASE**

surface. After several minutes, spontaneous reagglomeration of these particles took place. Repeated tests to uncover some surface active agent on these particles proved negative. In experiments aimed at determining the reason for this particle behavior UO_2 particles were spread on water over a permanent magnet placed 1/8 inch beneath the water's surface. Observation of modified spreading behavior gave a clue to the reason for the particles' reagglomeration. A small sample of UO_2 particles was then examined for its iron content by atomic absorption techniques. These particles were found to have $100\mu\text{g}$ of iron per gram of UO_2 (ORNL). Magnetic action by this amount of iron could easily explain the reaggregation of the spread particles; the original spontaneous spreading is not as readily explained.

Spreading of UO_2 particles using the dry spreading aid, acetyl cholinesterase, overcame the reagglomeration and loss of the larger agglomerates which would otherwise sink when spread on water. UO_2 was mixed dry with acetyl cholinesterase flakes using a flamed (but cool) platinum wire, and when applied to the air/water interface, this mixture flashed out with the particles, rigidly

holding them in place. When prepared TEM grids of this preparation were examined, a loss of the larger UO_2 particles by interaction with the electron beam was noted. Further studies on this approach were discontinued with UO_2 after it was verified that the UO_2 particles were held rigidly in the film but contained no significant quantities of submicron particles in the preparation as delivered. UO_2 powder with many submicron particles became available later in the project, through the cooperation of Dr. R. Kaiser of Avco Corporation, but were not evaluated by this technique.

It was thus demonstrated that considerable particle separability could be achieved as a result of introducing particles to the air/water interface without any other source of energy. Complete particle deagglomeration by interfacial forces was not usually attained due to the gross techniques used to prepare the mixture and to introduce the particle to the interfaces. If the agglomerates were first mechanically broken down so that the particles were initially separated and then solidified in a polymeric material, then as this material is introduced to the air/water interface individual particles would spread and be held in the spread film. We were usually able to supply sufficient mechanical energy to deagglomerate the particles by sonication* in a volume phase and then spread these particles at the air/water interface. A series of experiments of this type was completed in which the deagglomerated material was mixed with a thin-film forming agent, as discussed in the next section.

3.1.5 Particles First Dispersed in Wetting Agents with Polymeric Agents Added for Spreading and Stabilization of Interfacial Films

In the following paragraphs, the use of a primary energy source to initially break down agglomerates in a wetting liquid containing a surface-active film-forming material is discussed. Several materials were used in these experiments; however, in all cases the initial particle deagglomeration was done by ultrasonically treating the particle mixture for several minutes. Visual observation of carbon agglomerates sonicated in chloroform, having some added poly-benzyl-glutamate, clearly showed that these agglomerates were very

*Sonication is used to connote ultrasonically dispersed.

readily reduced in size. The following materials were spread, with their burden of ultrasonically separated particles, under varying conditions in the Langmuir trough to produce films of separated particles:

- a. Stearic acid in chloroform
- b. Cytochrome C in water
- c. Poly-benzyl-glutamate in chloroform
- d. Poly-methyl-glutamate in DCA* and chloroform
- e. Collodion in amyl acetate
- f. Poly-L-Lysine in water

In comparison studies with a few of these materials, two special experiments were run. In one, the particles were added directly into the spreading mixture and then stirred prior to spreading at the air/water interface. The second experiment ultrasonically treated the particle mixture before introduction to the air/water interface. In all cases, the particle-spreading solution mixture was introduced to the air/water interface over the surface of a pre-wetted glass slide used as a ramp. This was done so the particle mixture gently merged with the air/water interface in a controlled way, thereby minimizing particle loss from the interfacial film.

Table I contains detailed information on the spreading of particles in PBG^f and chloroform, and for comparison, particles in a collodion plus amyl acetate mixture.

A large variety of such experiments did not reveal a satisfactory "universal" method in which mixtures of particles of diverse origin can produce films of completely separated particles at the air/water surface. One example of failure to separate particles spread in this way is shown in Figure 15, from an experiment in which calibrating carbon was ultrasonically dispersed in a PBG and chloroform mixture and then spread on the water surface.

* DCA=Dichloro Acetic Acid

f
PBG = poly benzyl glutamate

Table I
SUMMARY OF EXPERIMENTAL RESULTS USING
PBG + CHLOROFORM SPREADING SOLUTION

TYPICAL EXPERIMENT	PURPOSE	USUAL RESULT
SPREAD 0.1 MG OF PBG IN 0.1 CC CHLOROFORM AT AIR/WATER (A/W) INTERFACE.	TO ESTABLISH A RELATIONSHIP BETWEEN SPREADING PRESSURE AND SURFACE AREA OF PBG FILM.	THE PBG FILM FORMED BY SPREADING 0.1 MG PBG WAS EXTREMELY STABLE, EASILY WITHSTANDING A 5 DYNES/CM FILM PRESSURE. IT WAS DECIDED THAT THIS FILM WAS THICKER THAN NECESSARY AND THAT A SOLUTION OF 0.5 MG/CC PBG WOULD BE ADEQUATE.
SPREAD ULTRASONICALLY DISPERSED CALIBRATING CARBON IN 0.5 MG/CC PBG CHLOROFORM AT CLEAN WATER SURFACE.	TO DETERMINE IF ULTRASONIC ENERGY COULD SEPARATE AGGLOMERATED PARTICLES PRIOR TO SPREADING.	THE EM GRIDS USED TO SAMPLE PARTICLES SPREAD UNDER THESE CONDITIONS WERE RAISED THROUGH THE WATER/FILM/AIR INTERFACE WHEN THE COMPRESSION FILM PRESSURE WAS 2 DYNES/cm. ELECTRON MICROSCOPIC EXAMINATION OF THESE GRIDS SHOWED 2-DIMENSIONAL AGGLOMERATES CONTAINING 5 TO 100 PARTICLES. THE PARTICLES WERE RIGIDLY HELD IN PLACE BY THE PBG FILM INDICATING THE BENEFIT OF THIS FILM MATERIAL. IN ADDITION, THE REMAINDER OF THE SPREAD PARTICLES WITHIN THE FILM COULD BE COLLAPSED INTO A FILAMENT WHICH COULD BE ARCHIVED FOR FUTURE PARTICLE EXAMINATION.
CARBON PARTICLES ADDED DIRECTLY INTO 0.5 MG/CC PBG IN CHLOROFORM AND SPREAD AT AN A/W INTERFACE. THE PARTICLES WERE STIRRED PRIOR TO SPREADING.	TO DETERMINE IF THE SPREADING FORCES PRESENT AT THE A/W INTERFACE WERE SUFFICIENT TO BREAK DOWN AGGLOMERATES WITH NO PRIOR ULTRASONIC AGITATION.	THE EM GRIDS WERE PICKED UP AT 2 DYNES/CM COMPRESSION FILM PRESSURE AS ABOVE. THE PARTICLES OBSERVED ON THESE GRIDS WERE BASICALLY 3-DIMENSIONAL AGGLOMERATES. VERY FEW 2-DIMENSIONAL AGGLOMERATES WERE OBSERVED.
CARBON PARTICLES ULTRASONICALLY DISPERSED IN 0.5 MG/CC PBG IN CHLOROFORM AND SPREAD AT AN A/W INTERFACE.	TO DETERMINE PARTICLE SEPARATION RESULTING FROM ULTRASONIC ENERGY AND THE BENEFITS OF AN EMBEDDING FILM.	POLYETHYLENE WAS USED TO RETRIEVE THE SPREAD SAMPLE BY LAYING THE POLYETHYLENE ON THE WATER'S SURFACE AND PEELING BACK WITHOUT EXTERNAL SURFACE PRESSURE. PARTICLE CLUMPS WERE OBSERVED THAT WERE STUCK TOGETHER BY PBG FILM MATERIAL.
CLAY PARTICLES ADDED DIRECTLY INTO 0.5 MG/CC PBG IN CHLOROFORM AND THEN SPREAD AT THE A/W INTERFACE. MIXTURE WAS STIRRED PRIOR TO SPREADING OF PARTICLES.	TO DETERMINE THE SEPARATION OF CLAY PARTICLES ACHIEVED AT THE A/W INTERFACE.	THE EM GRIDS WERE PICKED UP AT 6 DYNES/CM COMPRESSION FILM PRESSURE. EXAMINATION OF THE EM GRID SHOWED POOR PARTICLE SEPARATION. MANY OF THE CLAY PARTICLES WERE COLLECTED ON THE GLASS SPREADING RAMP SHOWING A NEED FOR BETTER APPLICATION TECHNIQUE FOR THESE NOMINALLY HYDROPHILIC PARTICLES.
CLAY PARTICLES WERE ULTRASONICALLY DISPERSED IN 0.5 MG/CC PBG IN CHLOROFORM AND SPREAD AT THE A/W INTERFACE.	TO DETERMINE IF ULTRASONIC ENERGY COULD PRODUCE PARTICLE BREAK-UP WHICH WOULD BE ACCENTUATED BY SPREADING AT THE A/W INTERFACE.	EM GRIDS WHICH WERE PICKED UP AT A COMPRESSION FILM PRESSURE OF 5 DYNES/CM REVEALED VERY SPARSE PARTICLE DENSITY. PARTICLE SEPARATION WAS POOR BUT DIFFERENT FROM THAT OBSERVED WITHOUT ULTRASONIC TREATMENT.
UO ₂ PARTICLES ULTRASONICALLY DISPERSED IN 0.5 MG PBG IN CHLOROFORM AND THEN SPREAD AT THE A/W SURFACE.	TO DETERMINE IF ULTRASONIC ENERGY COULD IMPROVE PARTICLE SEPARATION AND STABILIZE THE FILM FORMED AT THE A/W INTERFACE.	EM GRIDS WERE PASSED THROUGH THE WATER SURFACE AT 5 DYNES/CM FILM PRESSURE. THE EXAMINATION OF THESE GRIDS REVEALED FEW UO ₂ PARTICLES.
ThO ₂ (ALFA) ADDED INTO 0.5 MG/CC PBG IN CHLOROFORM AND SPREAD AT A/W INTERFACE.	TO CHECK SEPARATION OF THIS MATERIAL USING SPREADING FORCES AT A/W INTERFACE.	THE EM GRIDS WERE PASSED THROUGH THE WATER SURFACE AT A COMPRESSION PRESSURE OF 2 DYNES/CM. MOST ThO ₂ PARTICLES SANK WHEN APPLIED TO THE WATER SURFACE. EXAMINATION OF THE EM GRIDS REVEALED THAT FEW PARTICLES WERE RETRIEVED.
ThO ₂ (ALFA) WAS ULTRASONICALLY DISPERSED IN 0.5 MG/CC PBG IN CHLOROFORM THEN SPREAD AT THE A/W SURFACE.	TO DETERMINE IF THE SPREADING OF THESE PARTICLES COULD BE ENHANCED BY DISPERSING IN THE BULK OF THE SOLUTION.	THE EM GRIDS WERE PASSED THROUGH THE WATER SURFACE AT A COMPRESSION PRESSURE OF 5 DYNES/CM. MOST PARTICLES WERE OBSERVED TO SINK WHEN SPREAD ON WATER. EXAMINATION OF THE EM GRIDS REVEALED VERY FEW PARTICLES IN THE RESULTANT INTERFACIAL FILMS.
CALIBRATING CARBON ULTRASONICALLY DISPERSED IN COLLIDION IN AMYL ACETATE.	TO DETERMINE IF PARTICLE SEPARATION COULD BE MAINTAINED ON A/W INTERFACE USING A FILM MATERIAL.	THE SPREAD MATERIAL WAS PICKED UP ON A PREPARED TEM GRID UNDER CONDITIONS OF NO EXTERNALLY APPLIED PRESSURE. IT INDICATED THAT THE CARBON PARTICLES WERE STILL AGGLOMERATED AND ALSO GLUED TOGETHER BY THE COLLIDION.

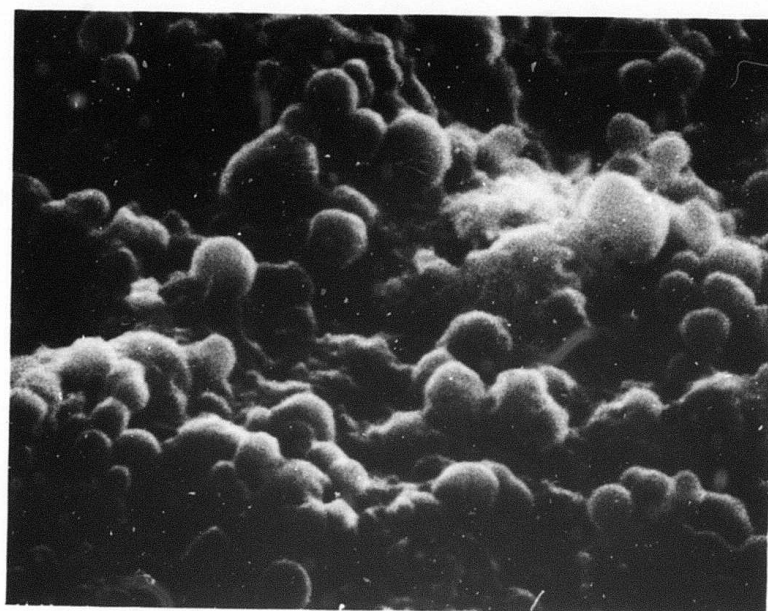
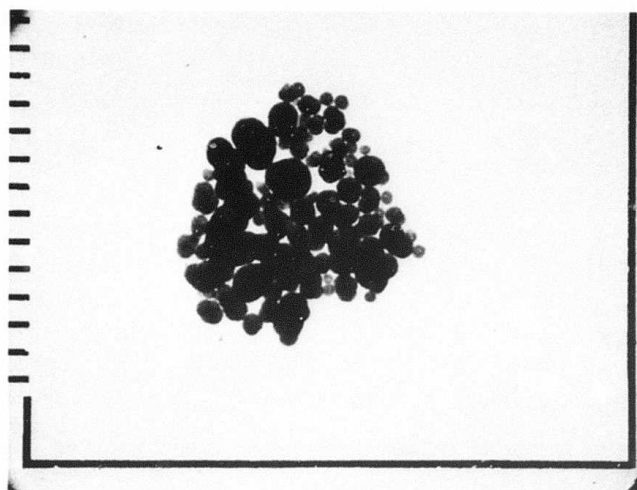


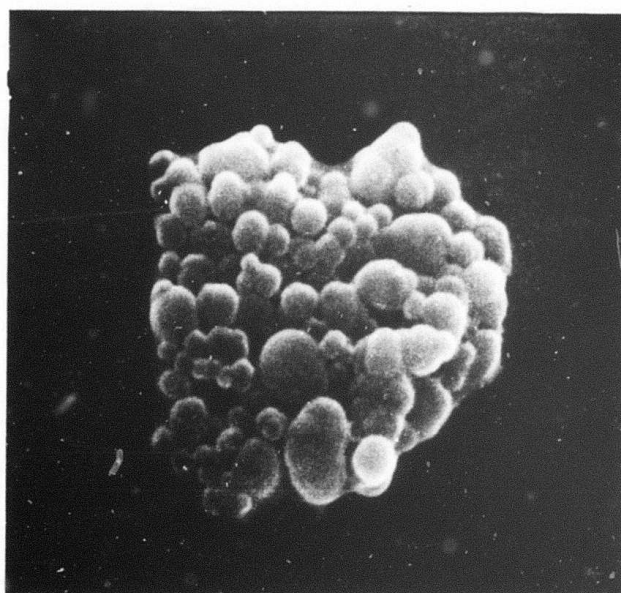
Figure 15 SEM VIEW OF CALIBRATING CARBON PARTICLES SPREAD ON WATER FROM MIXTURE OF PBG + CHLOROFORM, PICKED UP ON POLYETHYLENE

The calibrating carbon particles appear to have been stuck together by the PBG film material, a result which was later demonstrated to reflect the rapid aging of the spreading solution with a greater percentage of the particles behaving as shown in Figure 15 with increasing time of storage.

Additional evidence of this effect was observed with carbon particles ultrasonically dispersed in a collodion + amyl acetate mixture. When spread on the water surface, the visual appearance was extremely favorable; however, examination in the electron microscope revealed the presence of many three-dimensional agglomerates. A selected area was chosen and imaged in the scanning electron microscope. Figure 16 shows these views. The collodion film is readily seen in the SEM view (B) of these particles.



a) TEM VIEW



b) SEM VIEW

Figure 16 SEM AND TEM VIEWS OF SOME CALIBRATING CARBON PARTICLES AFTER MIXING WITH COLLODION AND AMYL ACETATE AND SPREADING AT AIR/WATER INTERFACE

Thus, although the use of ultrasonic energy was shown to be capable of deagglomerating material, the simultaneous presence of polymeric film forming agents added to the mix was favoring reagglomeration of the particles.

3.1.6 Ultrasonic Treatment of Materials in Liquid Spreading Aids Only

In this series of experiments, the particles were first ultrasonically dispersed in at least one of the following liquids.

- a. chloroform
- b. amyl acetate
- c. water
- d. butanol
- e. Siliclad*

Ultrasonic treatment times of five to fifteen minutes proved adequate to produce good colloidal suspensions of a variety of particles.

Calibrating carbon, as well as most other materials investigated, was given various pretreatments such as increasing its surface energy by exposing the particles to a glow discharge in air at reduced pressure. This surface activation was done while the particles were being agitated in an electrodeless glow discharge system. The apparatus used to surface activate the particles is described in Calspan Report No. 176,** available upon request. This treatment will make most materials hydrophilic.

Ultrasonic treatment of calibrating carbon in water produced a good particle dispersion only when the particles*** were first surface activated by

* Siliclad - a product of Clay Adams Division of Becton Dickinson and Co., Parsippany, N.J. 07054.

** Electrodeless Glow Discharge Cleaning and Activation of High-Energy Substrates to Insure Their Freedom From Organic Contamination and Their Receptivity For Adhesives and Coatings; Calspan Report 176.

*** Calibrating Carbon is hydrophobic - GDT renders the particles hydrophilic so that they disperse more readily in water.

glow discharge treatment (GDT). However, this material would sink when introduced to the air/water interface because of the absence of any spreading aids and its easy wettability by the subphase liquid. This mixture was placed in an atomizer and sprayed on a prepared TEM grid. Figure 17 shows a view of carbon particles treated in this manner.

The degree of particle separation, as shown in Figure 17, was unusually low and was not anticipated; therefore, additional experiments were performed to characterize the particle suspensions prior to spreading. In these experiments, drops of the spreading mixture were placed directly on as prepared TEM grids and simply allowed to air dry. Figure 18 is a typical area as seen on the TEM grids from these experiments.

Particle separation, as shown in Figure 18, was better than that seen in most other techniques tried prior to that date. To further improve on this, it was reasoned that a faster drying liquid would result in less particle reagglomeration when sampled by placing a drop of the mixture on a prepared TEM grid.

Mixtures of calibrating carbon dispersed separately in chloroform, amyl acetate and butanol were experimented with. Figure 19 shows a typical area of a prepared TEM grid on which a drop of the chloroform mixture was placed.

When sampling a mixture of this type, it was necessary to use the carbon coated side of the prepared grid; otherwise, the plastic substrate material was damaged. With carbon coated Formvar grids, some of the Formvar was dissolved by the chloroform, tending to adversely glue the particles together.

This view of carbon particles shown in Figure 19 is typical; however, some areas where the particles formed a two-dimensional array were also usually present.

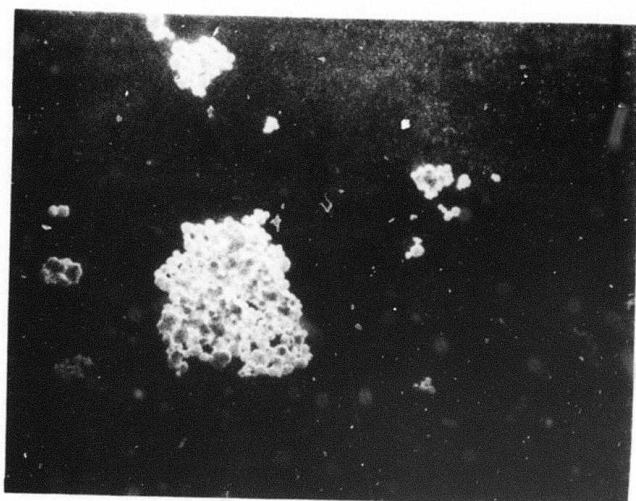
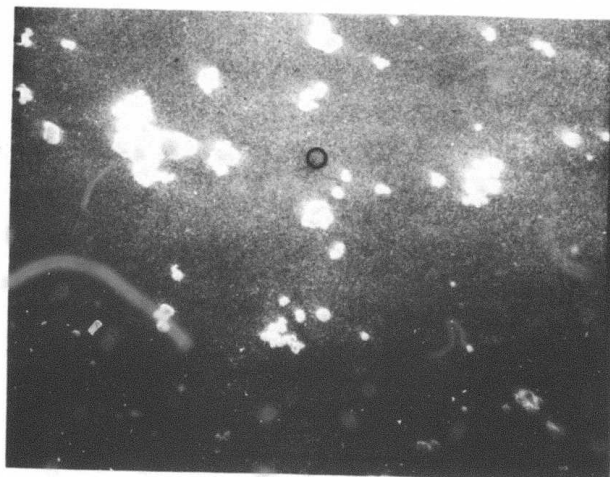


Figure 17 CARBON PARTICLES ULTRASONICALLY DISPERSED IN WATER AND ATOMIZED ONTO A PREPARED ELECTRON MICROSCOPE GRID

→ | ← 1 μ m

Figure 18

CARBON PARTICLES ULTRASONICALLY DISPERSED IN WATER AND PLACED DIRECTLY ON A PREPARED TEM GRID AND SET TO AIR DRY



→ | ← 1 μ m

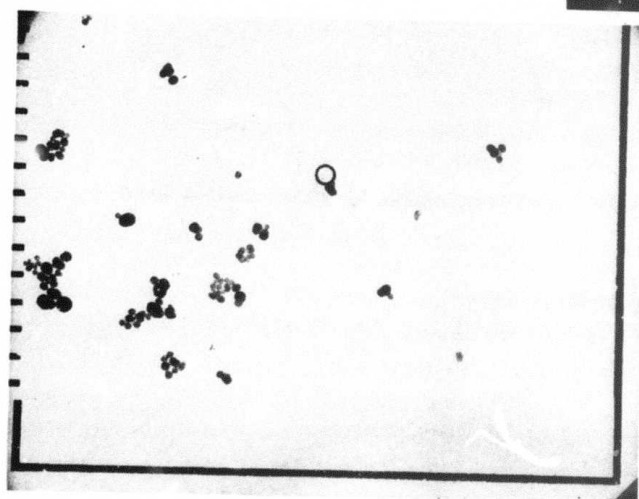


Figure 19 TYPICAL VIEW OF CARBON PARTICLES FROM DROP OF A SONICATED CARBON PARTICLES AND CHLOROFORM MIXTURE

→ | ← 1 μ m

For comparison, calibrating carbon dispersed in amyl acetate and sampled in the same way is shown in Figure 20.

Ultrasonically dispersing the particles in different solutions appeared to have definite benefits as one lengthed the time they remained suspended. For example, a dispersed mixture of carbon particles in butanol contains many particles in suspension even after nine days of settling. Figure 21 shows carbon particles prepared from a butanol suspension.

The views in Figures 19, 20 and 21, indicate the best routine particle separation obtained. The technique of ultrasonically dispersing the particles in a fast drying wetting agent and then using this mixture as the starting material to be spread at the air/water interface accomplishes two very important goals. First, it separates particles from each other and secondly it arrays the particles in a plane.

As a demonstration of this secondary two-dimensional distribution, the agent used to achieve particle separation was a commercial surface active preparation for siliconizing glassware called Siliclad, a concentrated liquid which can be diluted with water. In our work, the liquid was used to coat all particles placed in it and then, when spread on water, the mixture flashed out to produce the desired particle separation while preventing the particles from sinking because once spread they would not be wet by water.

Early experiments showed that calibrating carbon agglomerates exhibited poor particle separation on water when concentrated Siliclad was used. This was traced to the very rapid spreading of Siliclad with respect to the particles. Also, the solubility of Siliclad in water depleted the surface film as the spread layer was compressed prior to sampling. When 50% water-Siliclad mixtures were made as the suspending fluid media, calibrating carbon agglomerates (added to this solution and ultrasonically treated for 5 minutes to give a well-dispersed mixture) spread at the air/water interface to give typical arrays of particles

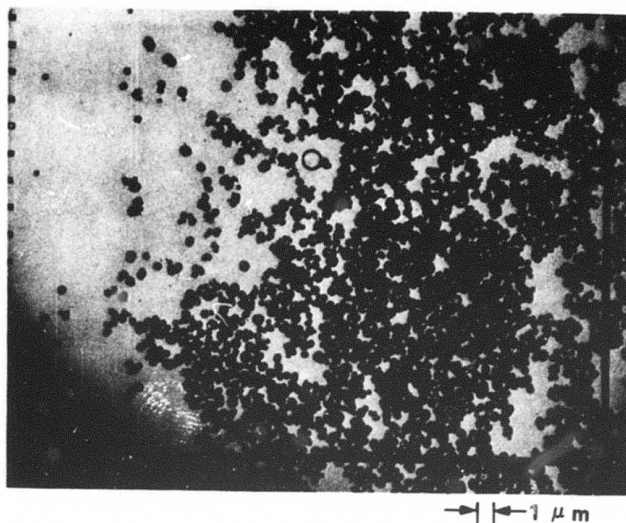


Figure 20 TYPICAL VIEW OF CARBON PARTICLES FROM A DROP OF A SONICATED CARBON PARTICLE + AMYL ACETATE MIXTURE

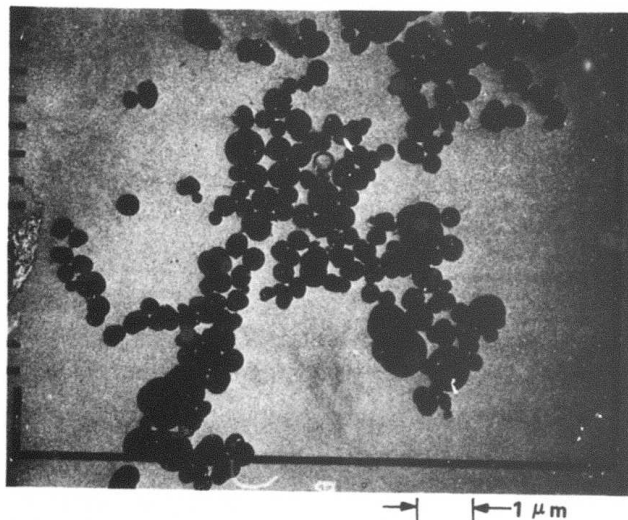
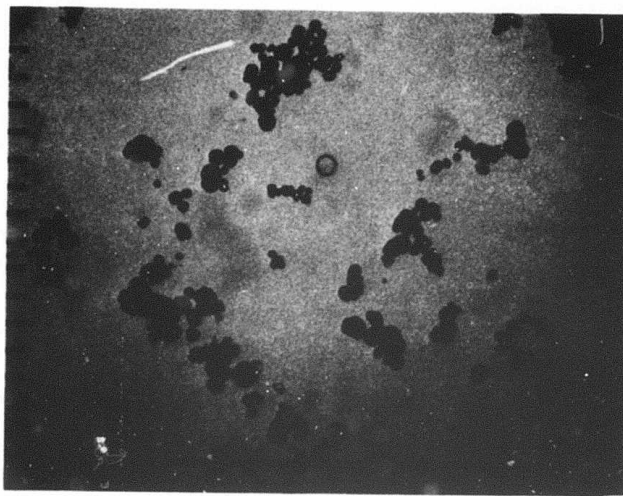


Figure 21 TYPICAL VIEW OF CARBON PARTICLES FROM A DROP OF A SONICATED - CARBON PARTICLES IN BUTANOL MIXTURE SETTLED FOR NINE DAYS

illustrated in Figure 22. The particle separation produced by this technique is not complete. However, it is a significant improvement over the separation of particles produced when applied directly to a prepared TEM grid, where the particles interacted and clustered together.



**Figure 22 CALIBRATING CARBON PARTICLES IN A 50%
WATER-SILICLAD MIXTURE ULTRASONICALLY
TREATED FOR 5 MINUTES AND THEN SPREAD
AT AIR/WATER INTERFACE**

3.1.7 Summary of Results Using The Air/Water Interface To Achieve
Particle Deagglomeration

Use of the air/water interface to achieve particle deagglomeration without the use of any spreading aids or support films did not prove successful. This conclusion was reached based on results with essentially pure materials. The fact that weathered materials do indeed appear to spread at clean air/water interfaces does not imply they are undergoing significant agglomerate breakdown, but rather that the organic contaminants on weathered particles (as shown in Section 3.5) serve to spread the agglomerates as such on the water

surface. The addition of liquid and/or dry film spreading aids (which mimic the spreading of a weathered sample) to the particle agglomerates was, similarly, insufficient to cause particle deagglomeration when these mixtures were spread at the air/water interface.

Deagglomeration of particles is best produced by preliminary ultrasonic dispersion of the particles in various fast drying liquids. This was established by sampling these dispersed mixtures directly on prepared TEM grids. A scheme for extracting these separated particles from the volume phase of a liquid and displaying them on a plane surface suitable for examination has been developed. Originally, this scheme was conceived for the initial spreading of particles mixed with dry spreading aids onto the water surface of a small water trough using a strip of aluminum foil as a carrier. This foil would also serve as the substrate on which the spread particles would be deposited. A laboratory version of this device was constructed. However, it did not prove useful for its original purpose when studies showed that dry spreading aids alone could not separate the particles. This device is shown in Figure 23. In using this device, the material to be deagglomerated is placed on the aluminum foil at position A. With a hydrophilic aluminum surface, this material will spread and/or float as the foil is pulled slowly downward through the water trough. As the material is spread, it will be picked up onto the emerging aluminum foil at position B (by the Langmuir-Blodgett film transfer mechanism) as it is rolled out of the water. A second foil material (I) is then interleaved with the collecting aluminum foil. This interleaving material serves to prevent contact of the retrieved particles with the back of the aluminum foil.

One major difficulty with this technique is a redistribution of the particles transferred to the hydrophilic substrate that occurs during the time it takes the water to evaporate. To overcome this, it is necessary to introduce a "binder" film at the gas/liquid interface to rigidly fix the spread particles in place. A protein film works well, allowing the hydrophilic substrate as

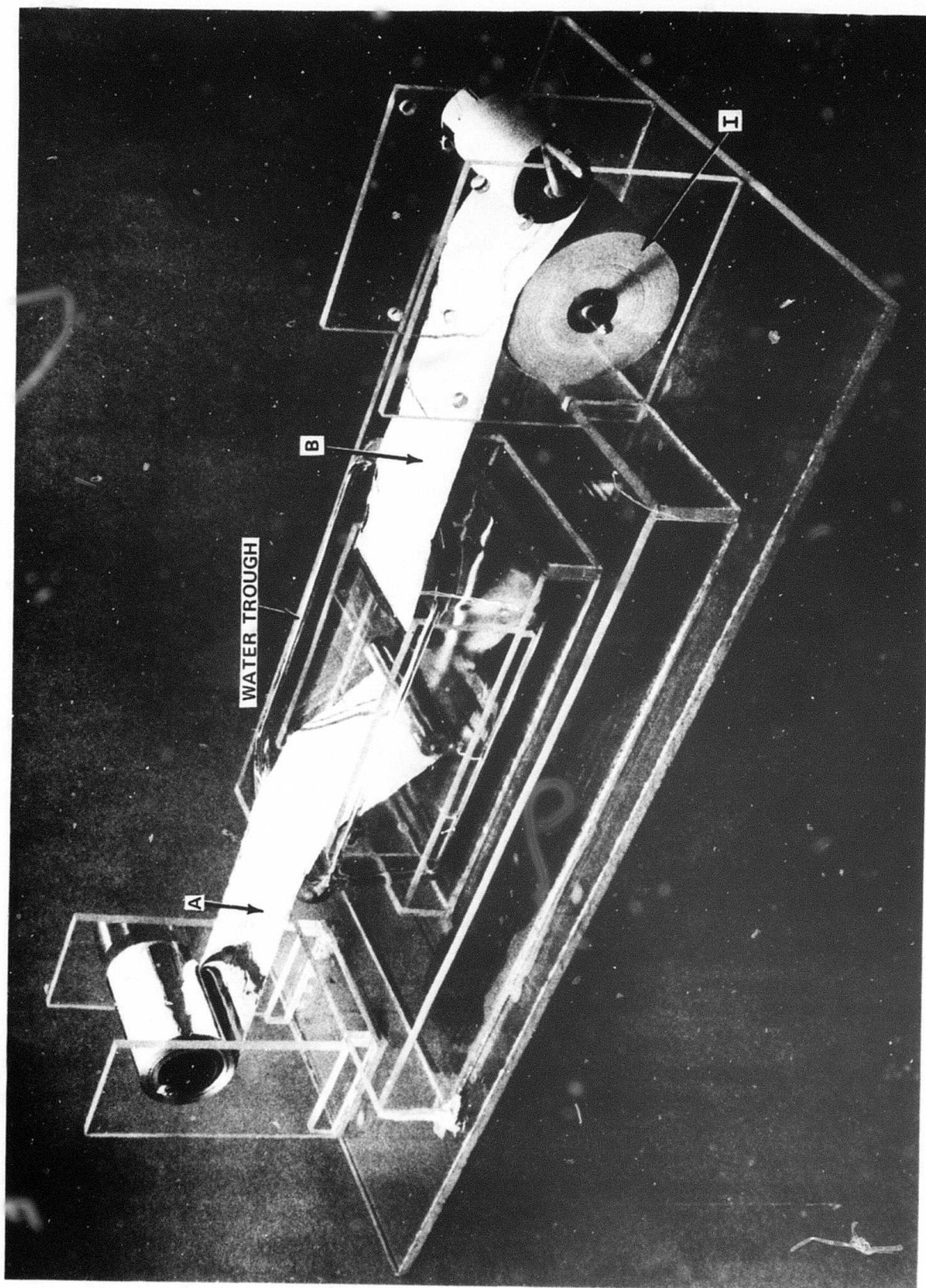


Figure 23 PROTOTYPE OF PARTICLE SEPARATION DEVICE USING LANGMUIR-BLODGETT FILM TRANSFER MECHANISM

withdrawn through the water surface to dry with the particles rigidly fixed in place. Typical steps in using this technique are summarized below:

1. Mix 5 mg of agglomerated particles in a small test tube with 15 ml of wetting liquid.
2. Ultrasonicate the particle-liquid dispersion for 15 minutes.
3. Allow 4 hours for settling out of the larger particles.
4. Spread 2 drops of this dispersion at the clean air/water interface and let stand for 15 minutes.
5. Introduce a protein solution below the water surface and let stand for 15 minutes.
6. Prepare a hydrophilic substrate, preferably by glow discharge treatment; Lexan (polycarbonate) is a good choice.
7. Insert this treated sheet into the water surface and withdraw slowly.
8. Examine the sheet from Step 7 in the SEM after gold coating.

Figure 24 shows the result of preparing UO_2 particles by this technique. It is expected that further development of this technique which couples ultrasonic dispersion and air/water interfacial separation will yield the most useful results.

3.2 SEPARATION OF PARTICLES USING INTRINSIC WETTING PROPERTIES

Using sonification to deagglomerate particles proved to be extremely useful as part of the technique discussed in Section 3.1.6. This section deals with an extension of the sonification technique wherein methods based on surface chemical properties are investigated to separate particles of all types.

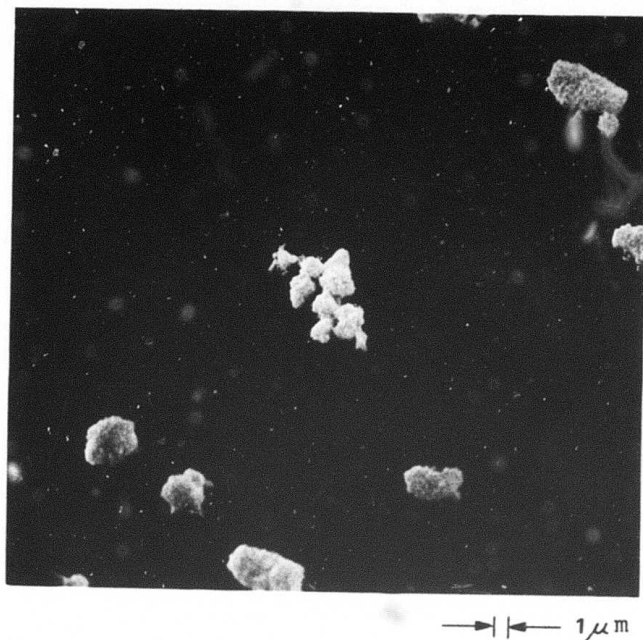


Figure 24 UO₂ PARTICLES PICKED UP ON LEXAN FROM WATER SURFACE

For example, if particle type A is wetted by solution a, it will then disperse in a. Now, if two particles are present in the original mixture, e.g., type A and B where B is not wetted by a, then the settling or floating of B is used to separate it from A. Furthermore, if A is broken up into smaller parts A_1 , A_2 , A_3 , then this technique serves to deagglomerate and to separate particles of different types. Figure 25 depicts some of the approaches followed in this study. The glow discharge treatment step has not been used often as it imparts high surface energy to most materials, thereby precluding their separation by variations in wettability.

Experiments involving the use of chloroform and water to separate particles on the basis of their hydrophobic or hydrophilic surface properties are also reported in this section. Initially, mixtures of particles of differing types were experimented with. This was followed by separation of similar type particles using the same techniques.

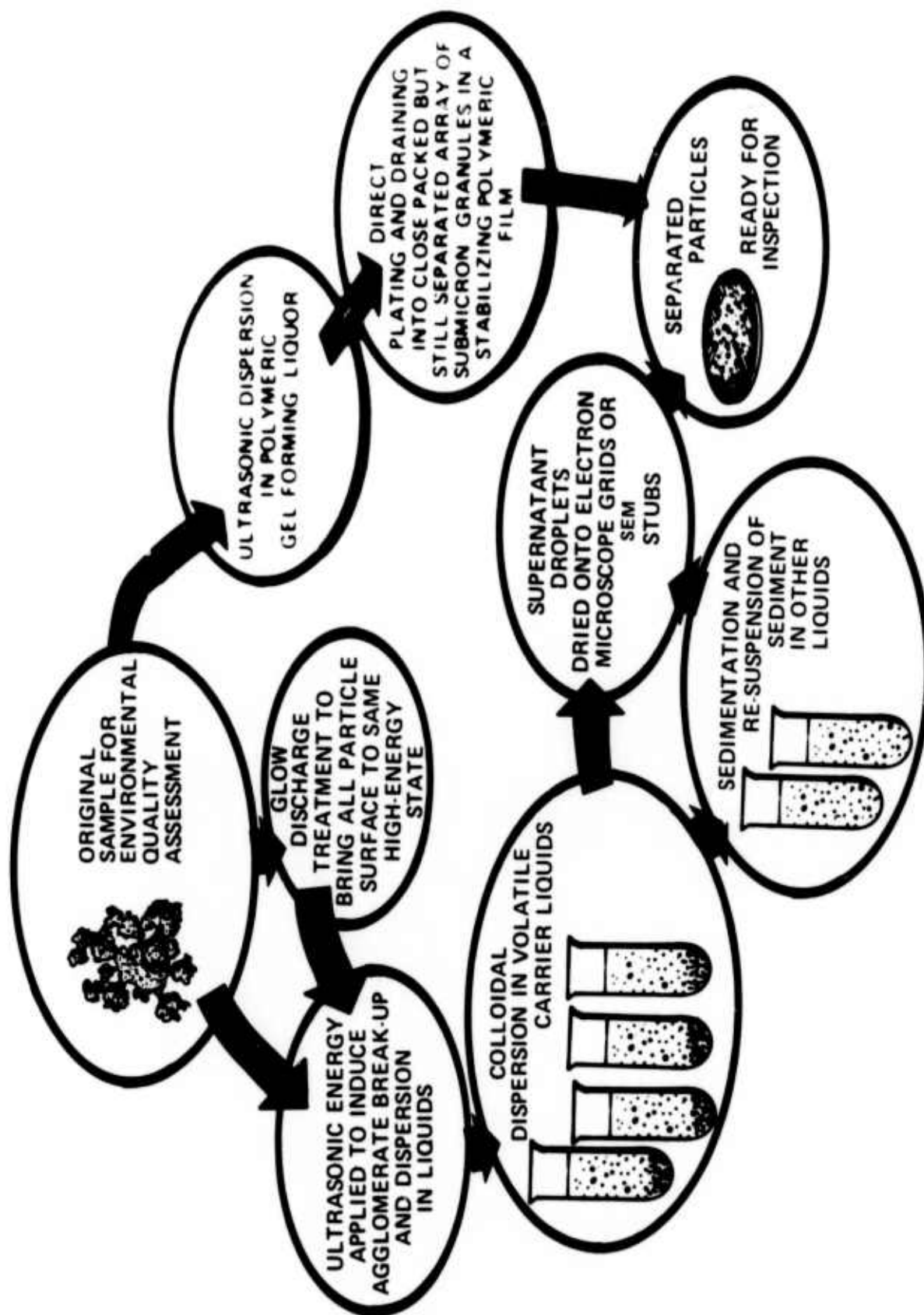


Figure 25 SEPARATION OF PARTICLES USING THEIR WETTING PROPERTIES

3.2.1 Separation of Two Materials According to Wetting Properties

Calibrating carbon and kaolin clay were used as the two primary particle types in the initial experiments. It was expected that carbon would disperse well in chloroform and it would settle out in water; the clay was expected to disperse well in water and settle out in chloroform.

The experimental procedure was to add a mixture of clay and calibrating carbon to distilled water and chloroform in separate containers. These particles were then dispersed by ultrasonically treating the particle/liquid mixtures. After a period of time, samples of the supernates were taken in order to sample the particles in suspension. Sampling was accomplished by placing a drop of the supernatant on prepared electron microscope grids and examining them in the transmission electron microscope (TEM).

The material that settled at the bottom of each mixture was then redispersed in the opposite liquid medium. The two steps in particle preparation are illustrated below:

Step I: A few milligrams of calibrating carbon and kaolin clay were ultrasonically dispersed in 25 ml distilled water in a small beaker. A similar mixture was ultrasonically dispersed in 25 ml chloroform in a small beaker. Both mixtures were stored for 16-18 hours so that particle settling would take place.

Step II: The settled residues from the solutions in Step I were collected and the remaining liquid allowed to evaporate. The residue from chloroform was redispersed in 25 ml of distilled water and then ultrasonically treated for 15 minutes. The residue from water was redispersed in 25 ml chloroform and also ultrasonically treated for 15 minutes. These mixtures were then covered and stored for 16-18 hours for particle settling.

Sampling Method

Samples for TEM examinations were taken from the specimens using a clean Pasteur pipet that was inserted just under the liquid surface in order to withdraw some supernatant. The third drop from the pipet was deposited on the support side of a prepared electron microscope grid. The electron microscope grid was then set aside in a clean area for air drying.

Method of Evaluation of Specimens

Twelve grid openings of each electron microscope grid were examined at random (no repeats) for the number of particles observed. The data collected reflect the degree of particle type separation, e.g., whether carbon and clay were present. This is indicated in Table II as the number of particles observed averaged over 12 grid openings. The degree of particle separation, i.e., whether particles of one type were single or clustered is indicated by the qualitative terms -- good, or fair, etc. The description good indicates that most of the particles of one type were observed singly.

Table II
SEPARATION OF PARTICLES ACCORDING TO HYDROPHOBIC
OR HYDROPHILIC SURFACE PROPERTIES

SAMPLE PARTICLES	STEP	CARBON PARTICLE SEPARATION	CLAY PARTICLE SEPARATION	NUMBER OF CARBON PARTICLES PER GRID OPENING	NUMBER OF CLAY PARTICLES PER GRID OPENING
MIXTURE OF CLAY + CARBON	I-CHLORO FORM	GOOD	GOOD	9	<0.5
MIXTURE OF CLAY + CARBON	I-WATER	NONE	FAIR	0	TOO MANY PARTICLES TO COUNT
MIXTURE CLAY + CARBON	II-WATER	GOOD	GOOD	6.5	3.3
MIXTURE CLAY + CARBON	II-CHLORO- FORM	GOOD	GOOD	5.5	2

The results were favorable enough to encourage attempts at similar separation of a quaternary mixture.

3.2.2 Separation of Four Materials According to Hydrophilic-Hydrophobic Properties

This series of experiments utilized the results of previous work that showed when a mixture of a hydrophobic and a hydrophilic substance is added to water and ultrasonically dispersed, the hydrophilic substance disperses in the liquid, while the hydrophobic substance does not. Conversely, when the same mixture is added to chloroform and dispersed, the hydrophobic substance disperses in the medium, and the other material settles out. These follow-up studies were designed to determine the possibility of separating 2 hydrophilic materials from 2 hydrophobic materials, and then separating them from each other of the same type.

In the original experiments, the hydrophobic substance used was calibrating carbon, and the hydrophilic was kaolin clay. The follow-up experiments used Teflon powder as the second hydrophobic and glass microbeads as the second hydrophilic substances. Figure 26 shows the experimental plan followed.

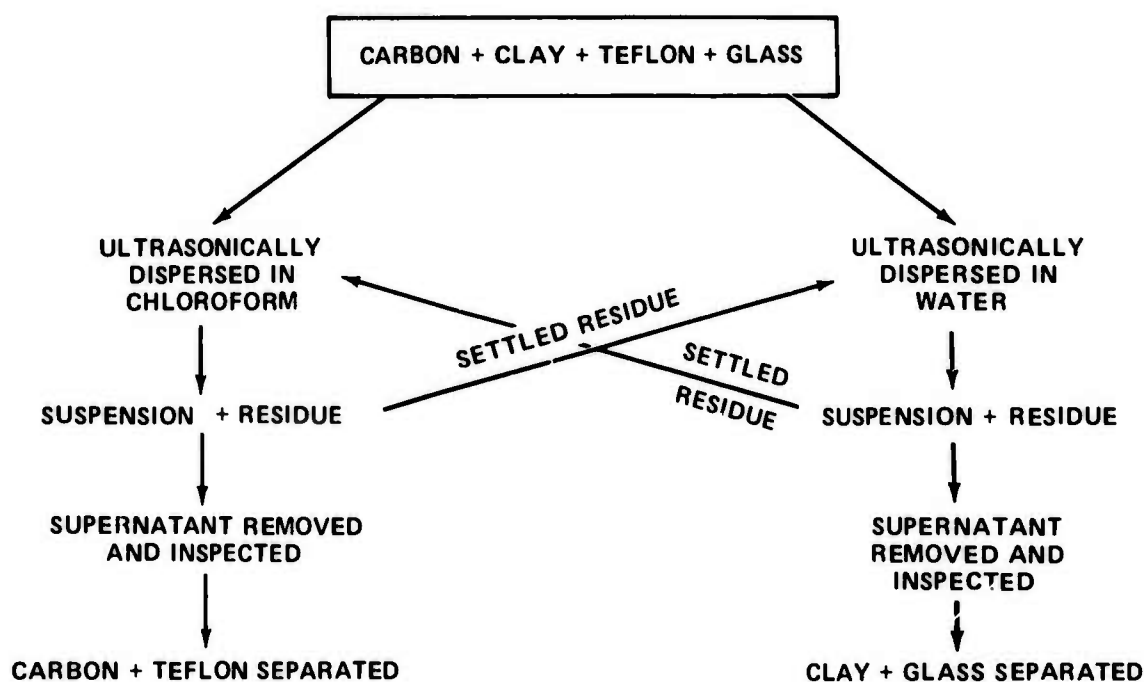


Figure 26 HYDROPHILIC-HYDROPHOBIC PROPERTIES EXPERIMENTAL PLAN

Techniques were the same as those in the first experiments: a few milligrams of powder were sprinkled into the liquid and ultrasonically dispersed for 15 minutes, covered and allowed to settle overnight. For sampling, the third drop of liquid taken from just below the surface was placed on the substrate side (except for CHCl_3) of an EM grid.

Preliminary Experiments

In six separate beakers, the following powders were dispersed in the specified liquids. Visual observations are recorded.

<u>Powder</u>	<u>Liquid</u>	<u>Description-after Ultrasonic Dispersion</u>
Microbeads	H_2O	light powdery layer on bottom, cloudy
Microbeads	CHCl_3	small amount on bottom, cloudy
Teflon	H_2O	floats on top
Teflon	CHCl_3	some visible on top, much on bottom
Clay + microbeads	H_2O	light powdery layer on bottom, some on top, cloudy
Teflon + carbon	CHCl_3	dark solution, "salt and pepper" mixture on bottom

Description of Grids

Microbeads in CHCl_3 :	no microbeads found on grid
Microbeads in H_2O :	good separation of beads
Teflon in H_2O :	small, opaque, irregular flakes
Teflon in CHCl_3 :	several large, crystalline flakes
Clay + microbeads in H_2O :	clay-bead separation - fair clay-clay separation - fair bead-bead separation - fair
Teflon + carbon in CHCl_3 :	There were very few "Teflon" flakes, and it is doubtful whether this was in fact Teflon.

Separation of all particles: Good

Summary Experiments

A mixture of the 4 powders was added to 25 ml CHCl_3 in one beaker and 25 ml H_2O in another. Each was ultrasonically dispersed for 15 minutes, covered and settled overnight.

Description of grids:

Mixture in CHCl_3 : Mostly carbon on each grid, clay being the next most predominant. There were a few groups of microbeads, and a few non-crystalline flakes (possibly Teflon). Separation was, in general, fair.

Mixture in H_2O : The entire grid was covered with fairly-well separated particles (no large clumps). Most particles apparent were microbeads and clay, both fairly well interspersed. Separation was fair to good. A few carbon spheres were also found on the grid.

Final Results

Results with the aqueous medium were encouraging since, as expected, hydrophobic substances did not disperse (except carbon, to a small extent) in it, while hydrophilic substances did. Moreover, those that did disperse were fairly well-separated from each other. However, the expected opposite did not hold true. Hydrophilic substances not only dispersed in water, but, to some extent, in chloroform too. A further complication was that, apparently, Teflon was a poor choice for a "hydrophobic" substance, as its very low surface energy also rendered it "organophobic". It did not disperse in water, nor did it disperse in chloroform. Additional studies of a variety of suspending liquids are required for optimization of this technique.

This colloidal suspension technique has also been applied to actual separation of particulates collected in an air pollution filter sampler. Results of this work indicate that particles of different types are readily separated from each other depending on the liquid in which they are dispersed.

The majority of results described in this section were achieved using samples prepared only by direct placement of the colloidal suspensions onto electron microscope grids. This procedure has the disadvantage of allowing significant reagglomeration (when water is used as one of the liquids) and some "glueing" together of particles when chloroform is used (this attacks the support film of the TEM grid).

Two additional procedures show significant promise of allowing the excellent separations obtained in the volume phase of a colloidal suspension to persist when desiccated into a two-dimensional array (for inspection and particle analysis), as discussed in Section 5.

3.3 DEAGGLOMERATION USING HYDROPHOBIC, ABHESIVE OR UNSTABLE SURFACE-ACTIVE AGENTS

Figure 27 depicts two approaches which involve spreading the particles on a surface for examination and then, in situ, modifying the surface of the particles for further separation. Initial arraying of the particles for examination was done by sonification of the particles in butanol (BuOH) or chloroform, followed by spreading directly on a prepared TEM grid or a modified SEM stub. Subsequently, exposure of the particles under controlled conditions, to hydrophobic, abhesive, or hydrolytically unstable surface-active agents was carried out. Alternatively, the particles were exposed to high humidity to effect filmwise water condensation on the particles' surfaces and then subjected to rapid freeze/thaw cycling (equivalent to an accelerated weathering situation). In each case, the particles under study were monitored by visual observation in the SEM or TEM.

Typical experiments involved the use of octanol adsorption on the particles' surfaces with a subsequent exposure to high humidity or exposure of the particles to a silane vapor with subsequent exposure to high humidity. The freeze/thaw cycling experiments were carried out both with and without deliberate additives.

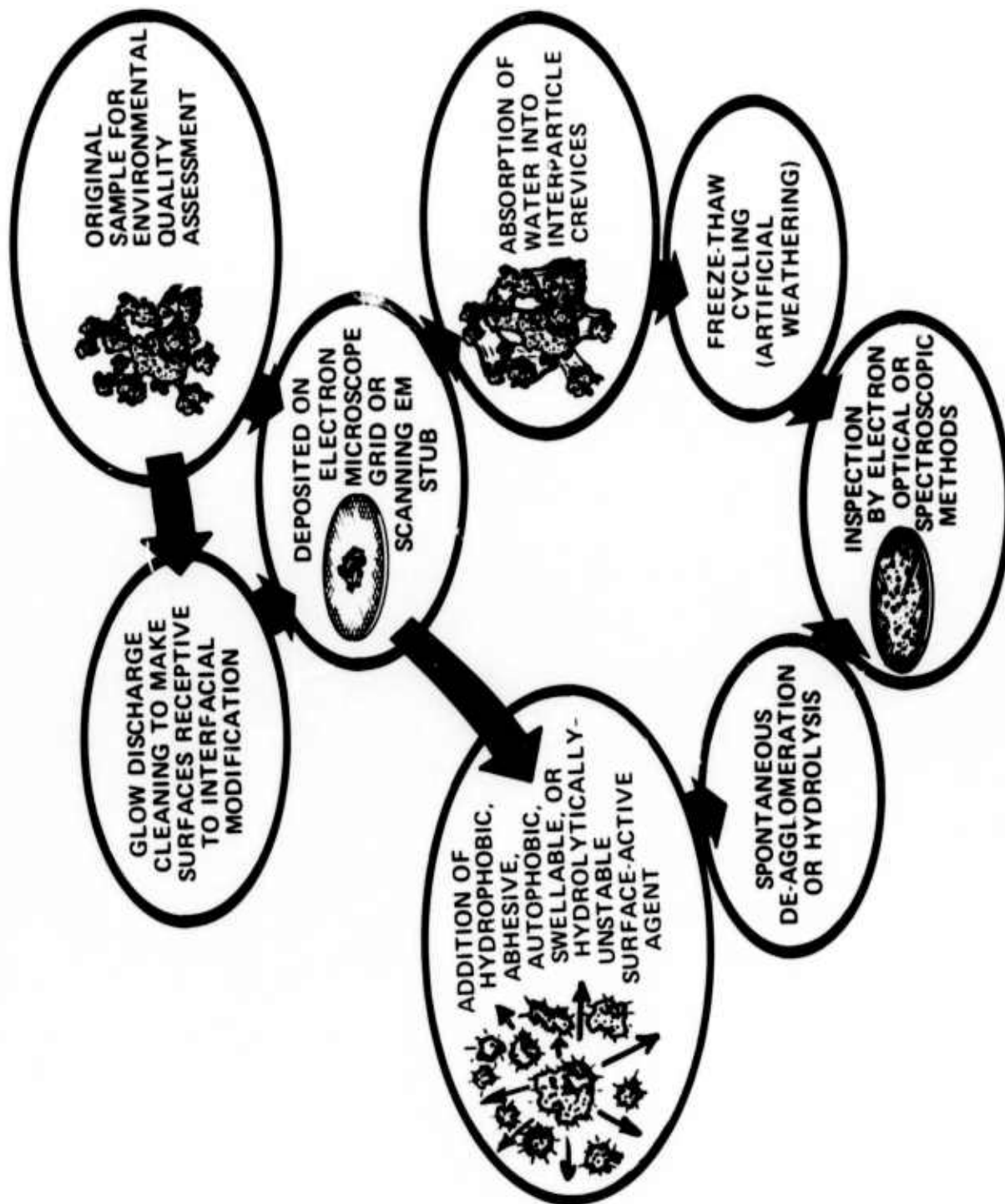


Figure 27 DEAGGLOMERATION USING HYDROPHOBIC, ADHESIVE OR UNSTABLE SURFACE-ACTIVE AGENTS

3.3.1 Particle Deagglomeration Using Hydrolytically-Unstable Surface-Active Agents

Deagglomeration of particles using autophobic surface active agents requires prior activation of the particles' surfaces followed by the adsorption of an organic surface-active agent and subsequent exposure of these particles to a high humidity condition.

In the paragraphs below, preliminary work required to activate the surface of the particles is discussed first, followed by an example using octanol as the autophobic surface active agent.

It was first necessary to develop a way to activate the particles without destroying the substrate on which they were placed. Since prepared TEM grids could not survive the glow discharge treatment, our scanning electron microscope was used to monitor the particles. Use of the SEM does not require transparent or fragile support substrates. Consequently, particles placed on a SEM stub should be present after glow discharge treatment (GDT), provided they are not destroyed in the process.

A special SEM stub was made that consisted of disk of Titanium 6V-4Al alloy attached to a regular aluminum SEM stub. A transmission electron microscope grid was then attached to the titanium alloy with Eastman 910 cement. Particles of natural ceramic grade UO_2 powder (from Dr. R. Kaiser of AVCO Systems Division, AVCO Corporation) were used in this work. UO_2 particles were placed in butanol* and ultrasonically dispersed for 5 minutes. A drop of the supernatant sufficient in size to cover a 3 mm TEM grid was placed directly on the indexed grid attached to the special SEM stub.

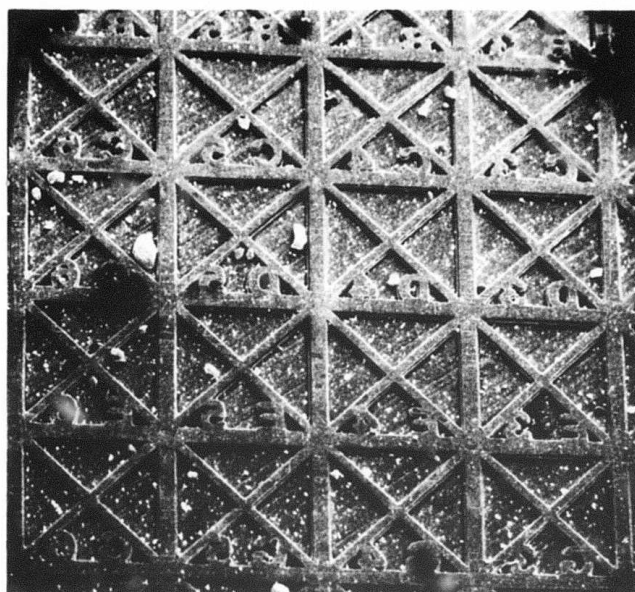
* Referred to as BuOH in Figures 28-33.

After the alcohol evaporated, the stub was examined in the SEM. Figure 28 shows selected particles at low magnification on the stub. Figure 29 shows the same area as in Figure 28 after GDT for 5 minutes. Repetitive microscopic examination of these samples showed that the larger particles were removed during GDT, and that such particles were not otherwise lost in handling.

Figures 30 and 31 at higher magnification show the same area before and after GDT.

Figures 32 and 33 show other regions of the copper index grid both before and after GDT. In this view, fine details within the copper grid are easily seen; however, UO_2 particles less than $0.5\mu\text{m}$ are not clearly resolved. One $0.5\mu\text{m}$ particle analyzed with our X-ray energy dispersive analyzer was shown to contain uranium. This is an important point since the electron beam used to generate the characteristic X-rays develops significant local heat. Figure 34 shows a magnified view of the region about the particles in Figure 32 and 33, but after gold coating the particles to improve image resolution. The UO_2 particle of interest is located by the intersection of coordinates indicated by the arrows in the border of these photos. The benefit of gold coating the specimen is clearly seen. A $0.08\mu\text{m}$ particle is easily resolved in Figure 34. With these results, it is clear that the particles will not be dislodged or removed by glow discharge treatment.

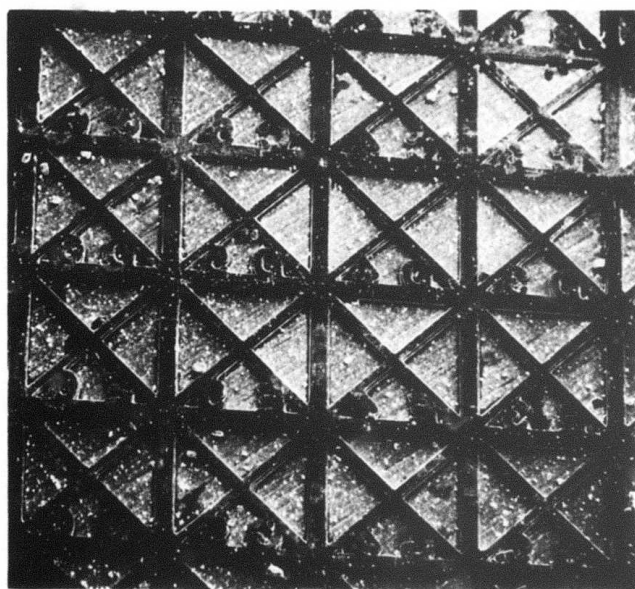
A chloroform dispersion of ceramic grade UO_2 powder gives acceptable initial particle deagglomeration. A few drops of this dispersion, applied to the special SEM stub, resulted in the distribution shown in Figures 35 and 36 before surface activation and application of the surface-active agent.



#1 UO_2 IN BuOH

→ | ← 100 μm

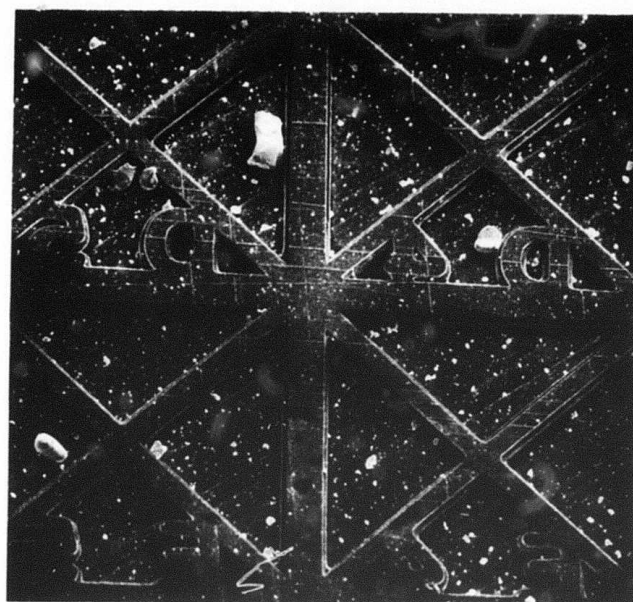
Figure 28 SELECTED PARTICLES OF UO_2 ON A SPECIAL SEM STUB



#1 GLOW (15 SEC) UO_2 IN BuOH

→ | ← 100 μm

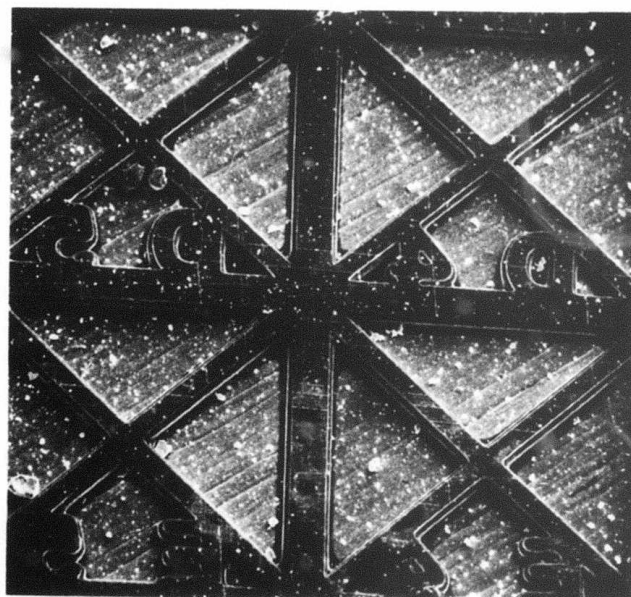
Figure 29 SELECTED AREA SHOWN IN FIGURE 28 AFTER GDT FOR 5 MIN



#2 UO_2 IN BuOH

→ | 100 μm | ←

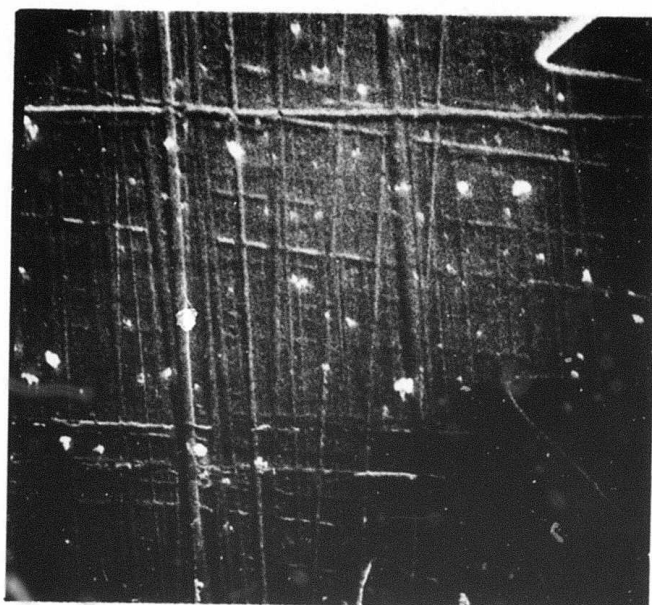
Figure 30 SELECTED AREA OF UO_2 PARTICLES BEFORE GDT



#2 GLOW UO_2 IN BuOH

→ | 100 μm | ←

Figure 31 SELECTED AREA OF UO_2 PARTICLES AFTER GDT



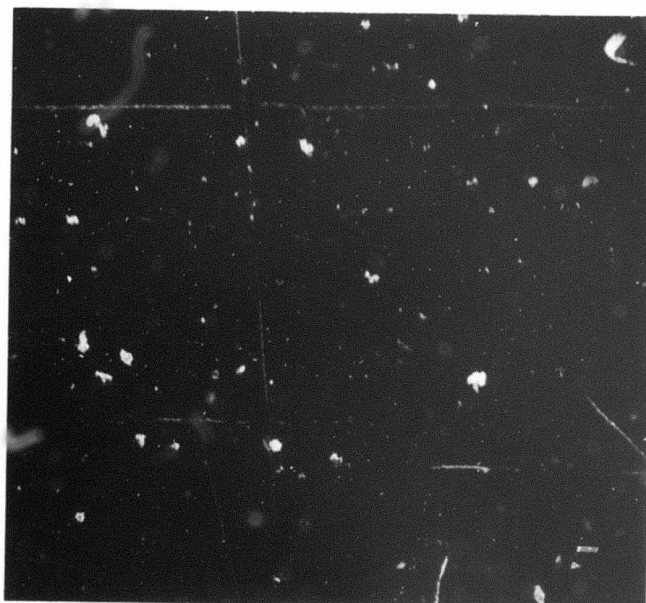
←
PARTICLE
ANALYZED

#4 UO₂ IN BuOH

→ || ←
1 μm

↑
PARTICLE
ANALYZED

Figure 32 MAGNIFIED VIEW OF UO₂ PARTICLES ON COPPER GRID



←
PARTICLE
ANALYZED

#4 GLOW UO₂ IN BuOH

→ || ←
1 μm

↑
PARTICLE
ANALYZED

Figure 33 MAGNIFIED VIEW OF UO₂ PARTICLES ON COPPER GRID AFTER GDT

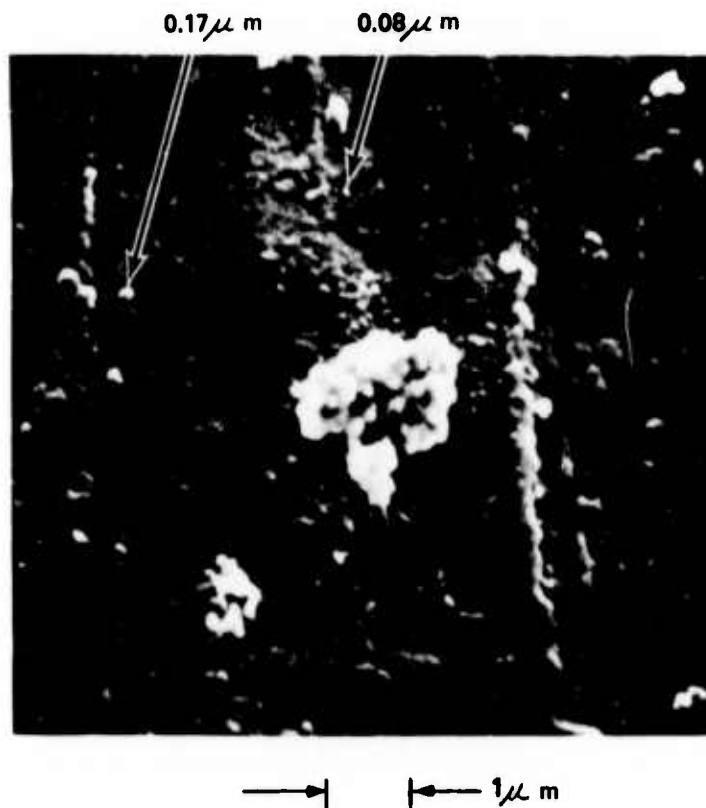


Figure 34 MAGNIFIED VIEW OF UO_2 PARTICLES AFTER GDT AND GOLD COATING

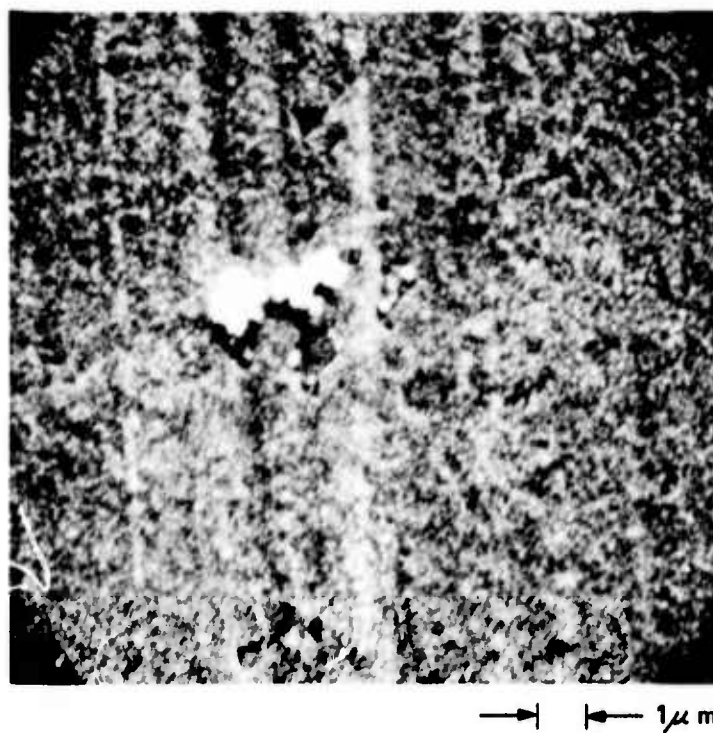
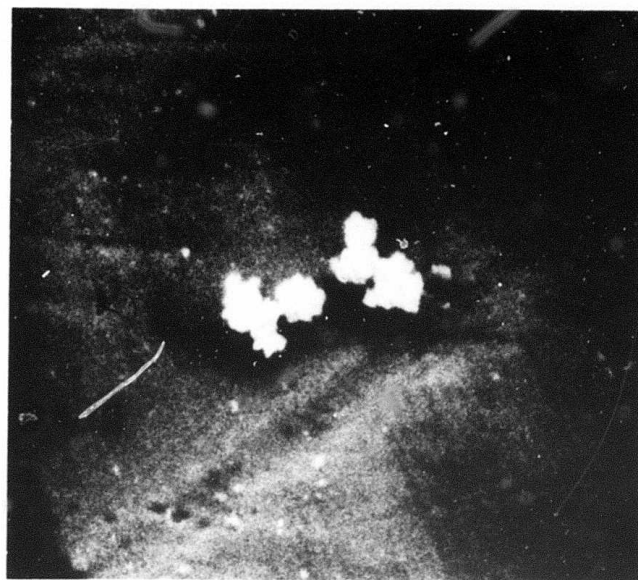
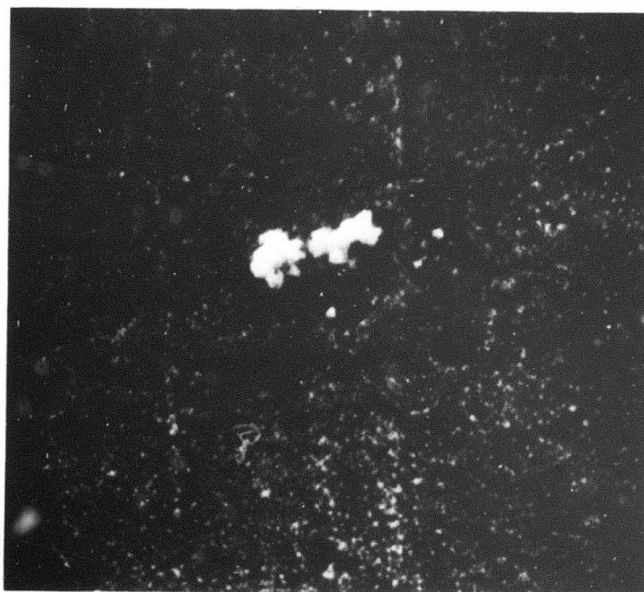


Figure 35 SELECTED UO_2 PARTICLES BEFORE SURFACE ACTIVATION



→ | ← 1 μm

Figure 36 SELECTED UO_2 PARTICLES BEFORE SURFACE ACTIVATION



→ | ← 1 μm

Figure 37 UO_2 PARTICLES IN FIGURE 35 AFTER SURFACE ACTIVATION AND TREATMENT – GOLD COATED

This special SEM stub was then inserted in our glow discharge apparatus and glow discharge treated for two minutes. After surface activation, octanol vapors were introduced into the glow discharge apparatus specimen tube without removing the activated specimen. This was done by bubbling argon through octanol for 30 seconds and venting the octanol vapors into the specimen tube. After this treatment, water vapor was introduced for 30 seconds into the specimen tube to bring about particle deagglomeration.

When this treatment was finished, the special SEM stub was removed and examined. Figures 37 and 38 show particles of UO_2 (as first shown in Figures 35 and 36) after treatment.

An examination of these figures reveals that the UO_2 particles did not deagglomerate. The reason for this could be that they were chemically bonded together and could not be separated except by mechanical comminution. Nevertheless, other experimental studies demonstrated only limited success with this separation technique.

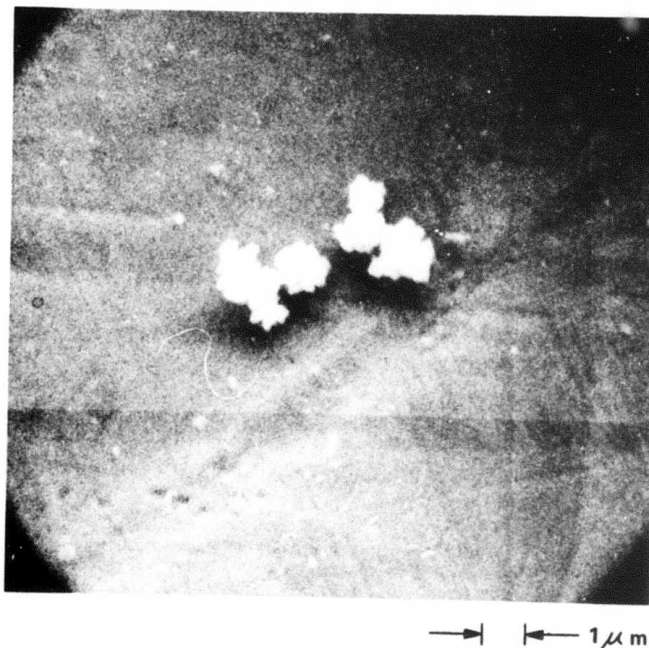


Figure 38 UO_2 PARTICLES IN FIGURE 36 AFTER SURFACE ACTIVATION AND TREATMENT - GOLD COATED

3.3.2 Particle Deagglomeration Using Hydrophobic Surface-Active Agents

In a typical case, in situ particle deagglomeration was initiated by exposure of the particles to silane* vapor. A small amount of calibrating carbon was ultrasonicated for 15 minutes in chloroform. One drop of this mixture was placed on a prepared TEM grid.

The positions of five different groups of particles were determined using the index markings on the grid. These groups were then photographed. The grid was then exposed to silane vapors by holding it for a few seconds over a heated beaker having a few cc of dimethylochlorosilane in it. (The spontaneous adsorption of silane vapors was checked by infrared spectroscopy.) After air drying the treated grid, the five areas of interest were re-examined. The results of this examination revealed that the silane treatment caused excessive damage to the grid support film and added much unwanted contamination.

The particle groupings, when compared to the photos taken before treatment, revealed no particle separation had taken place. In fact, the particles appeared to have been brought closer together. Thus, this approach to particle separation did not prove fruitful.

3.3.3 Particle Deagglomeration Using Freeze/Thaw Cycles

This scheme was based on the hypothesis that contacting particles might be separated by the expansion during freezing of layers of water molecules previously adsorbed to the particles' surfaces and in the capillary spaces between them.

In essence, this is an attempt to mimic nature, but in an accelerated fashion, in its comminution of particles. Fresh mixtures of 10 mg calibrating

* Silane - General Electric "Dri-film"

carbon in 20 cc chloroform were made for these experiments. Such mixtures were ultrasonically treated for 10 minutes after which the carbon formed a very dense suspension in the chloroform. Drops of such mixtures were transferred with a flamed platinum wire to the screened side of indexed prepared electron microscope (EM) grids. Such grids had been previously examined in the EM for contamination, and specific grid openings were denoted for this study.

After the particle-treated grids were dry, they were re-examined in the EM for carbon particles in the grid openings of interest. Areas were photographed representing the initial state of the chloroform + particle dispersion.

To subject the particles on the EM grids to freeze-thaw cycles, it was necessary to construct a small Plexiglas chamber to fit on a thermoelectric cooling device. This chamber could be alternately flushed with dry nitrogen gas or 100% humidified air. EM particle-containing grids to be treated were placed on aluminum foil in good thermal contact with the thermoelectrically cooled surface.

Humidified air was generated by bubbling dry nitrogen through water and then passing this gas over the EM grid. After the grid was treated for 5 minutes to achieve equilibrium conditions, the chamber was isolated and the thermoelectric cooler turned on. Grids were continuously examined at 200X during this time using a metallographic microscope.

No matter how slow the cooling operation was, condensed liquid water droplets formed readily on the copper EM grid and then solidified. After this was observed, the thermoelectric cooler was turned off and the EM grid flushed with dry nitrogen. The frozen liquid water droplets melted and then coalesced with other droplets into larger droplets which put the carbon particles through an air/water interface wherever particles were contacted by the advancing water drops.

The EM grids were then flushed with dry nitrogen until no liquid water could be seen. Grids were then examined in the areas previously selected for observation of particle separation. Direct observations of separate areas revealed that significant separation of the particles was not achieved during freeze-thaw cycles.

It appeared that film-wise condensation was not achieved on the particles' surfaces. In order to produce continuous water films, wetting aids were added to the water used to humidify the air passed over the EM grid. Both oleyl alcohol and a cationic detergent, Tri-Dodecyl Methyl Ammonium Chloride (TDMAC), were tried separately. In the case of oleyl alcohol, smaller water droplets were condensed than with water only; however, no significant particle separation was observed after a single freeze-thaw cycle. TDMAC-treated water produced even smaller water droplets; again, no separation advantages were obtained after repetitive freeze-thaw cycles.

The freeze-thaw cycling of particles as a means of producing particle deagglomeration is complicated by peripheral bulk water freezing which could counteract the interparticle water freezing forces. At this time, there does not seem to be any practical way to avoid this problem. In view of this, the freeze-thaw cycling of water-coated particles is discounted as a useful separation technique.

3.3.4 Summary

The various techniques discussed in this section to deagglomerate particulate materials have not met with success. In view of the technical difficulties in achieving the precise operating conditions under which these techniques might prove useful, they are not recommended for further study.

3.4 SUBSTITUTIONAL REPLACEMENT TO IMPROVE AND MAINTAIN PARTICLE DEAGGLOMERATION

Deagglomeration by substitutional replacement is a technique which depends upon prior volume separation of particles as achieved by ultrasonification of a material in a liquid. Steps in this technique are depicted in Figure 39. As shown earlier, ultrasonic dispersion by itself can be used to obtain good material deagglomerations. In this section, experiments aimed at improving and maintaining deagglomeration by the addition of particles of known size is discussed. In this separation scheme, it is accepted that a two-dimensional array of particles can be more easily achieved if they are allowed to be closely bordered or touched by other particles. If some or all of these bordering particles can be substituted with inert or secondary particles, then the particles of interest will be essentially isolated. For spheres of equal size, closest packing in a plane requires six nearest neighbors around each particle. If some or all of these nearest neighbors can be substituted for, then analytically useful separation will have been achieved. The ultimate separation which takes place or is possible depends, of course, on the surface chemistry of both the particles to be separated and the liquid in which they reside. The geometric separation or isolation scheme can utilize equal size particles, larger particles, or particles of a smaller size than the particles to be separated. Replacement particles of the smallest size also enhance the otherwise random substitution which would occur by particles of equal size. In the remainder of this section, two typical experiments are discussed in which particle separation by isolation was attempted using, first, submicron (300 Å - 500 Å diam.) silver halide particles and then by using particles of colloidal silica. The former has the added attraction of flagging radioactive particulates when photographically developed.

3.4.1 Particles of Interest Isolated by Surrounding Silver Halide Particles

In these experiments, submicron (300 Å - 500 Å dia.) silver halide particles were sonicated with calibrating carbon particles in an attempt

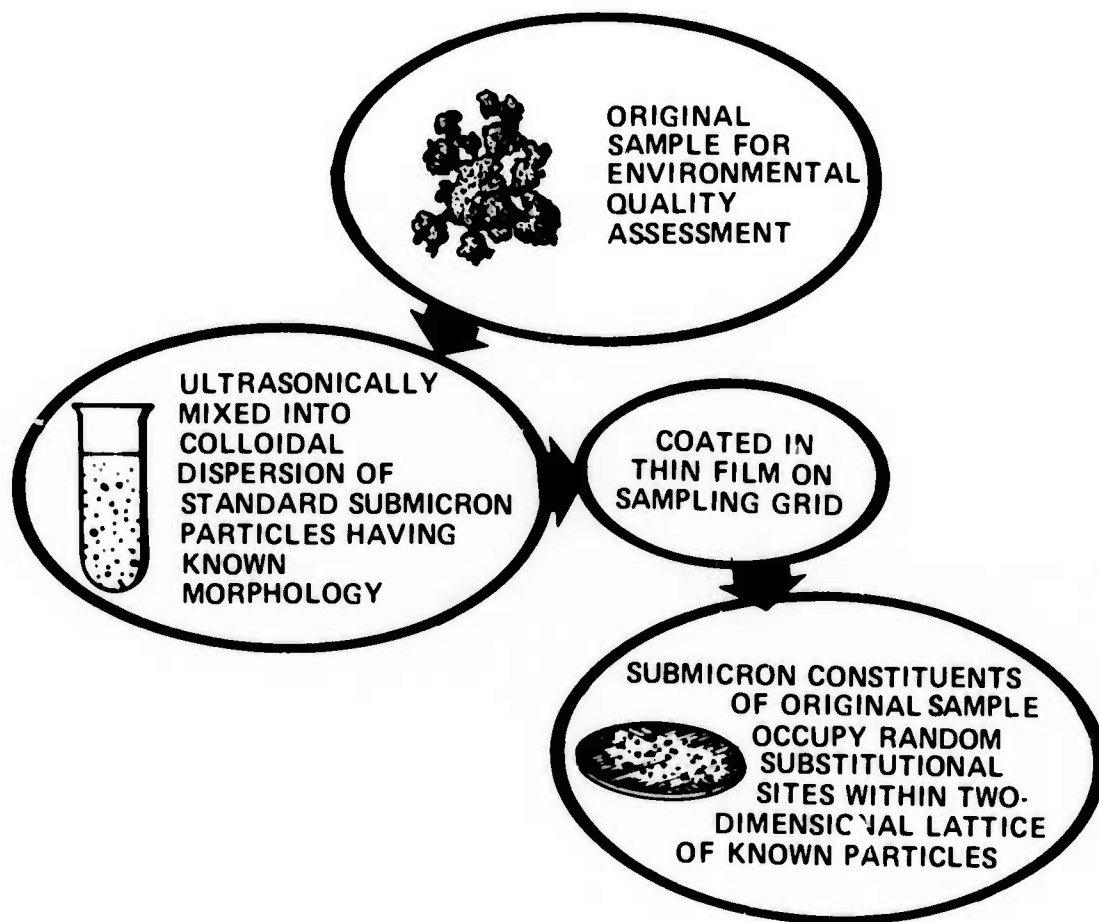


Figure 39 SUBSTITUTIONAL REPLACEMENTS TO IMPROVE AND MAINTAIN PARTICLE DEAGGLOMERATION

to preferentially surround the carbon particles with silver halide particles. An important feature of this technique is that the surrounding silver halide particles could also be used to locate radioactive materials by autoradiographic effects.

The experiment designed to test the usefulness of the technique followed a two-step plan. First, separation by isolation was attempted by producing a two-dimensional substitutional lattice of silver halide particles in which carbon particles dispersed. Second, when this test proved feasible, the autoradiographic aspects were briefly pursued.

Kodak Nuclear Track emulsion (NTE) was used for the source of silver halide particles. This material is supplied in a gelatin base which must be substantially diluted in order to achieve usable concentrations of silver halide particles. This is done by washing a small fraction of the concentrate several times in distilled water followed by centrifugation to concentrate the silver halide particles. In the first stage of the experiment, it was not necessary to work in the absence of light because only the separation aspect was sought.

A few milligrams of calibrating carbon were mixed with a few cc of water in which silver halide particles were concentrated. This mixture was ultrasonically treated for several minutes and then placed on a collodion-coated glass slide. The glass slide was immediately placed in a vertical position to allow the mixture to drain down the slide. The quantity of silver halide and gelatin was sufficient to produce a monolayer, which was confirmed by the uniform interference color on the dried slide. This film was scored into small squares and floated off onto water. Figure 40 shows an area which is typical on TEM grids used to pick up the specimen squares. The silver halide particles can be found between most of the carbon particles. This technique was investigated to the point where it appears feasible. However, a serious objection was raised to its general utility, since many carbon particles remained agglomerated by the action of the necessarily present gelatin. Attempts to use the inherent

film material, gelatin, as the support for the particles spread on the air/water interface were unsuccessful.

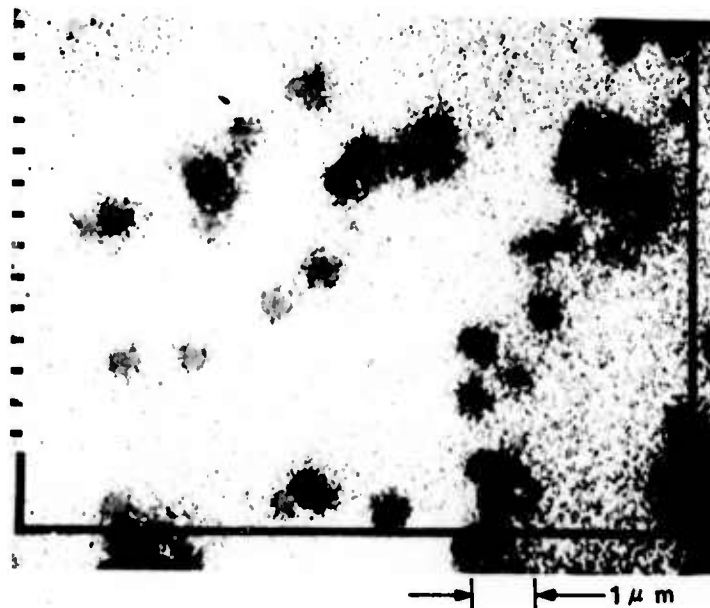


Figure 40 CARBON PARTICLES IN DILUTED NTE, ULTRASONICATED AND CAST ON A COLLODION COATED SLIDE (TYPICAL AREA)

Photographic development of the silver halide particles to determine which of the separated particles of real samples were radioactive was experimented with only briefly. No firm results were obtained. The developing procedure exposed the particles to many forces which could dislodge them from their substrate.

3.4.2 Particle Isolation in Collodial Silica

A 1% mixture of colloidal silica^{*} in water was prepared from a stock concentrated collodial silica solution. A drop of this diluted mixture was

^{*}Ludox - Colloidal Silica HS-40 in an alkaline solution. From E.I. DuPont DeNemours Co.

placed directly on a prepared TEM grid and when dried, examined. Very small particles, typically 100 Å, that were well separated from each other were found on the grid.

A few milligrams of calibrating carbon was then added to this 1% mixture. This was ultrasonically treated for three minutes, drops placed directly on prepared TEM grids, and examined when dry. It was found that the carbon particles were pasted together rather than being separated. Also a high degree of contamination was observed on the grids.

For a particulate sample containing many different types of particles, it may be necessary to use several types of known colloidal particles to achieve the required isolation. This would require extensive research into an area of questionable utility. From the preliminary results obtained, the technique seems to produce adequate separation to be pursued further, but with only modest further investment.

3.5 DEAGGLOMERATION BY REDUCTION OF PARTICLE SURFACE ENERGY

It was suspected that natural weathering of agglomerates might modify the particles surfaces in such a way that they would more readily deagglomerate when introduced to the air/water interface. In this section, results of experiments on natural and artificial weathering of particles are reported.

When particles are generated by any number of manufacturing processes, they are often in a very high energy state. Thermodynamically, this is an unstable condition which will approach stability through shape and surface chemistry changes of the particles. Typical shape changes involve particle agglomeration with other particles and typical surface chemistry changes involve the adsorption of energy lowering organic films on the particles. It is expected that the latter takes place more rapidly and, therefore, when the particles are agglomerated, they are already conditioned for separation by some technique which can still further lower the total energy of the system.

In order to test this hypothesis, samples of known particles can be removed from the environment and subjected to separation schemes. The approach used in this program was to work with both naturally weathered particles and with artificially "weathered" particles of known specifications.

3.5.1 Naturally Weathered Particles

Two sample groups, containing small quantities of originally pure particle types, were prepared in unsealed but rain-proofed containers and placed on the laboratory roof top. These materials were subjected to sun, wind, snow, rain and environmental air pollutants from the nearby municipal airport. It was the purpose of this exposure ("weathering") to determine if it would enhance or diminish particle separability.

Prior to being weathered, the materials in both groups exhibited poor two-dimensional spreading at the air/water interface.* The materials were delivered to the air/water interface by two techniques, by sprinkling and by lowering the material on a glass microscope slide through the surface of distilled water. Very little particle deagglomeration was observed in this initial work. The first group of particles listed below was weathered for 12 months.

Group 1

1. Glass microbeads
2. Kaolin clay
3. Aqua Nuchar (CARBON)
4. Alcoa Albon #552 nonleafing aluminum powder

These materials were placed separately in watch glasses fixed to the bottoms of plastic Petri dishes. Three holes cut in the top of each Petri dish permitted ample air circulation. A large Plexiglas cover was then placed

* A notable exception was UO_2 (ORNL) in Group 2.

over the top of -- but away from -- these Petri dishes to prevent direct rain and snow contact with the particles.

Figure 41 shows a top view of the particle weathering assembly for Group 1. The Plexiglas cover had been removed before the photograph was made. Also, the Petri dish cover had been removed from specimen 1. Group 2 specimens, discussed in Section 3.5.2, were weathered in a similar way.

Materials in Group 1 were characterized before weathering and generally fit the patterns described in Section 3.1 of this report. After one year of roof top "weathering", the following observations were made as listed by particle type.

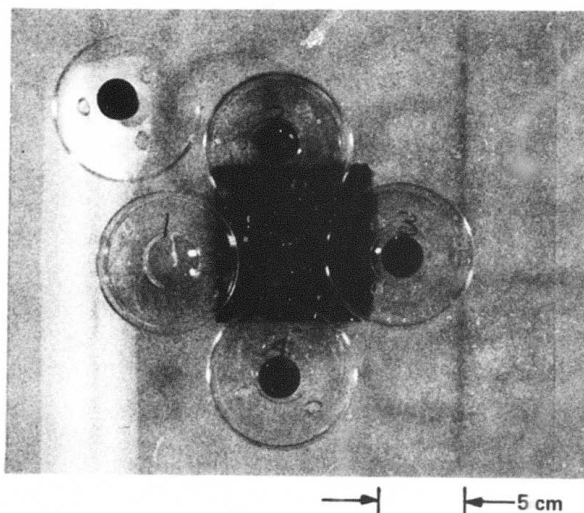


Figure 41 TOP VIEW OF PARTICLE WEATHERING SETUP

Glass Microbeads After Weathering - When this material was introduced to the water surface, most sank immediately. The material remaining on the surface was sampled and found to be low in particle concentration. These particles retrieved from the water surface were agglomerated. This weathered material behaved poorer in terms of its separability than did the pure specimens.

Kaolin Clay After Weathering - When sprinkled on the water surface, some of the material sank and some floated on the surface with no apparent surface activity. This material after weathering was significantly more agglomerated and resistant to separation.

Aqua Nuchar (Carbon) After Weathering - The unweathered material exhibited a delayed spreading on the water surface, ultimately forming a thick carbon carpet. With weathered material, no such spreading was observed. It appeared as if the carbon particles were agglomerated to a higher degree than when unweathered.

Alcoa Albon #553 Powder - This material behaved very similarly to the unweathered material when sprinkled on water.

Electron microscope grids were touched to the particle-coated water surfaces and droplets of the surface water containing the particulates allowed to air dry onto the carbon support film of each grid. Grids were touched at two different times, within one minute of the spreading and after the particles had been on the water surface for 30 minutes.

Specimen examination in the transmission electron microscope resulted in some interesting observations. It became apparent that the bulk of the material which flashed across the water surface was environmental contamination which had deposited in the watch glass. Some of these contaminants released small amounts of the originally clean powders. Typical contaminants observed follow.

- | | |
|-------------------|--|
| 1. Opaque spheres | similar to fly ash or glass microspheres; irregular surfaces |
| 2. Opaque spheres | a type which readily sublimates in the electron beam leaving evaporated crystals on the C substrate. |

- | | | |
|----|---------------------------|--|
| 3. | Translucent spheres | similar to a type of fly ash full of gas bubbles - a spherical porous mass |
| 4. | Transparent flakes | crystalline in nature - clay-like |
| 5. | Transparent larger flakes | amorphous in nature |
| 6. | Opaque flakes | too large to be carbon unless tight aggregates resulted from weathering |
| 7. | Porous flakes | crystalline in nature. |

A portion of the particulates which had reagglomerated on the surface of the water was picked up on a microscope slide and examined in a research metallograph microscope. Many of these contaminants were readily seen in this preparation. When viewed under polarized light, some spheres appeared to be glassy; some orange, yellow and green spheres and irregular particulates were also observed.

Scotch tape was then used to lift particulates from the surface of the bottoms of the Petri dishes in which the water glass sample holders were cemented. These particulates were also examined using the light microscope. Other contaminants were readily seen (e.g., wood fibers and insect parts).

The two observations made on these environmentally aged materials are in apparent disagreement. The disagreement is the difference between the spreading of the aged materials of interest and the contaminants found within the Petri dishes.

Apparently the sample holder was adequate for collecting environmental contaminants, but provided insufficient exposure of the test particles of interest to the surface-active environmental contaminants which would have aided in their separations.

The primary objective of this study was to determine if weathering as-received material would enhance or deteriorate the separability of the material. The weathering experiments as conducted did not establish this. If, in the life span of submicron particles from their original industrial emission to their final deposit, they have been effectively "weathered" as single particles prior to being collected as agglomerates, weathering should enhance the tendency of the agglomerate toward separation at an air/water interface. The crucial point is that effective single-particle weathering may only take place while the particles are airborne.

3.5.2 Sponsor-Supplied Materials

Five materials sent by the Air Force Technical Applications Center were characterized when received. The same materials were then again characterized after roof top weathering for three months. Preliminary characterization of these samples was done with a SEM. Specimens for these analyses were prepared by sprinkling the particles of interest on paper and then touching an adhesive sample stub to these sprinkled particles. The particles transferred to the stub in this way were then lightly metallized to provide electrical conductivity. Figures 42-51 illustrate typical results obtained from this preliminary study. Figure 42 shows the irregular crystal fragments seen in both the ALFA and ORNL thoria samples. Figure 43 shows a photo of ThO_2 at 20,000X with an indication of the particle surface. Whether the bumps on these particles are ultimately separable without the use of mechanical energy could not be determined in this program.

Figures 44 and 45 show SEM photos of spheres found only in the ORNL sample of ThO_2 . The chemical composition of these spheres was checked using energy-dispersive X-ray analysis. They were identified as a thorium compound, most likely ThO_2 .

SEM views of ORNL UO_2 particles are shown in Figures 46, 47 and 48. In these photos, the UO_2 particles clearly show a unique surface texture which sets them apart from the spheres seen in the ORNL ThO_2 .

The apparent holes in these spheres may result from gaseous decay products. Figure 48 presents an image recorded during attempts to look inside one of these holes; however, due to charging effects, this could not be done.

Figure 49 illustrates typical particle clusters seen in the sample of LiF at 1,600X. One special feature of this scanning electron microscope imagery was its revelation that some block like aggregates seen in the transmission electron microscope were in fact single particles. In the upper right hand side of Figure 49 the "aggregate" made up of a small cube on a larger one is clearly a single particle.

Figures 50 and 51 show SEM photos of CaF_2 with some indication of the presence of irregular elongated particles and small rounded particles adherent to spherical shaped particles of probably different composition.

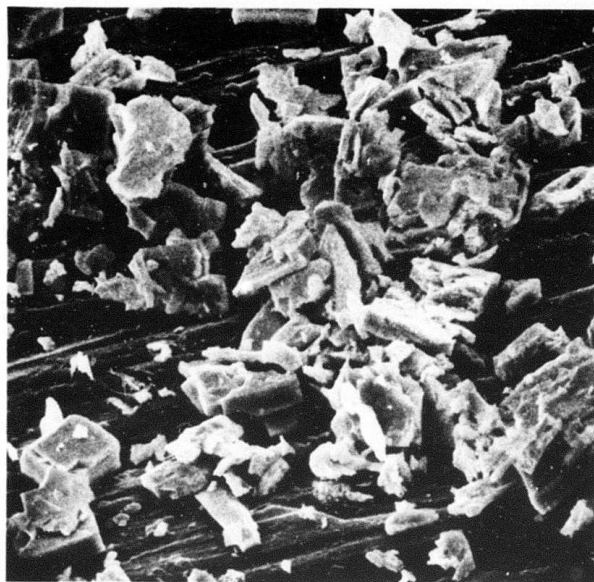


Figure 42 SEM PHOTO OF ThO₂ AT 1000X

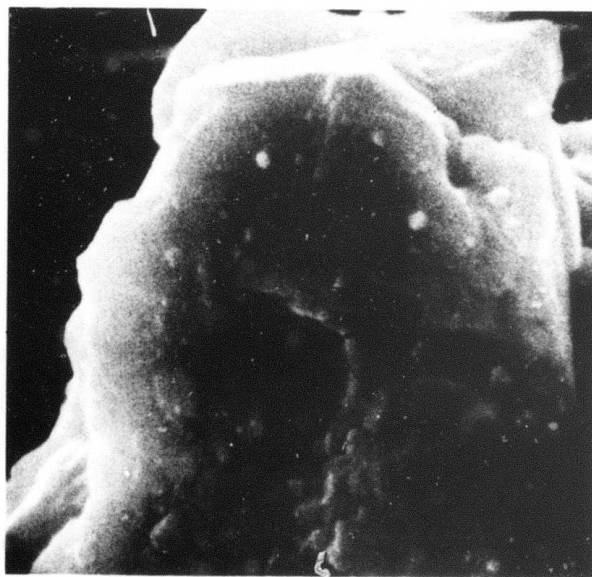


Figure 43 SEM PHOTO OF ThO₂ AT 20,000X

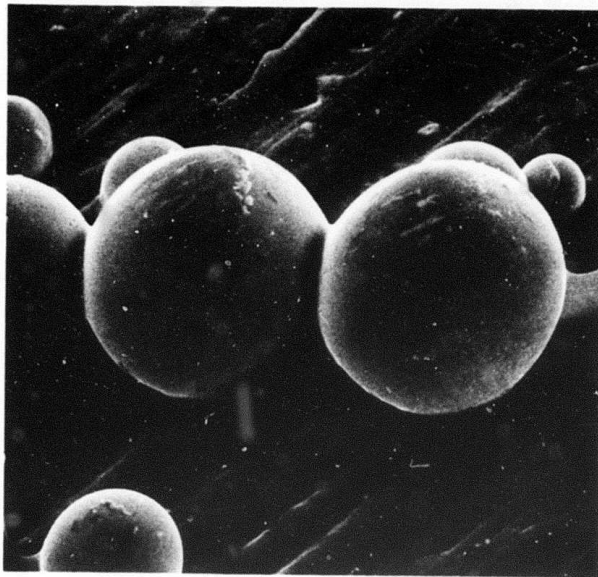


Figure 44 SEM PHOTO OF SPHERES FOUND IN ORNL ThO₂ AT 1000X

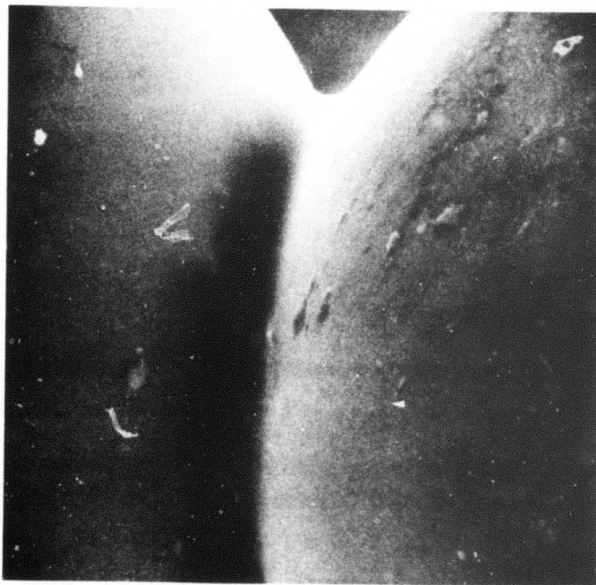


Figure 45 ENLARGED PHOTO OF SPHERES FOUND IN ORNL ThO₂ AT 5000X

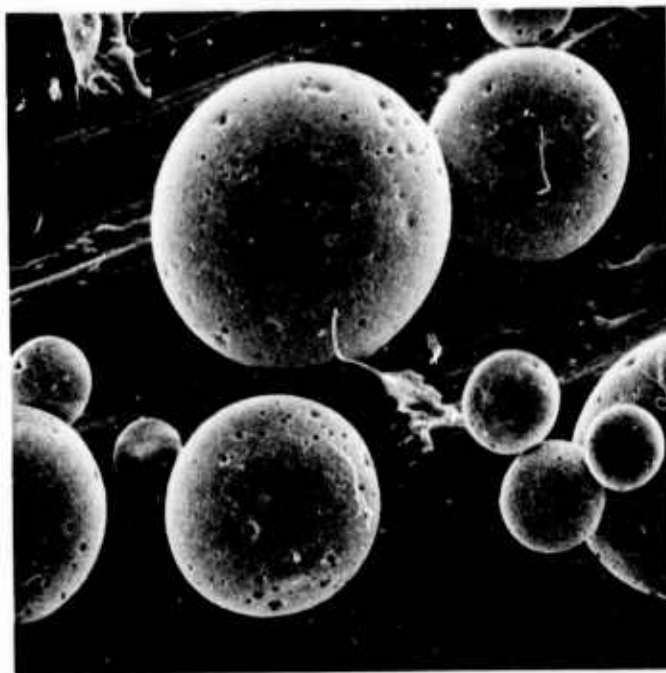


Figure 46 SEM PHOTO OF ORNL UO₂ AT 1000X

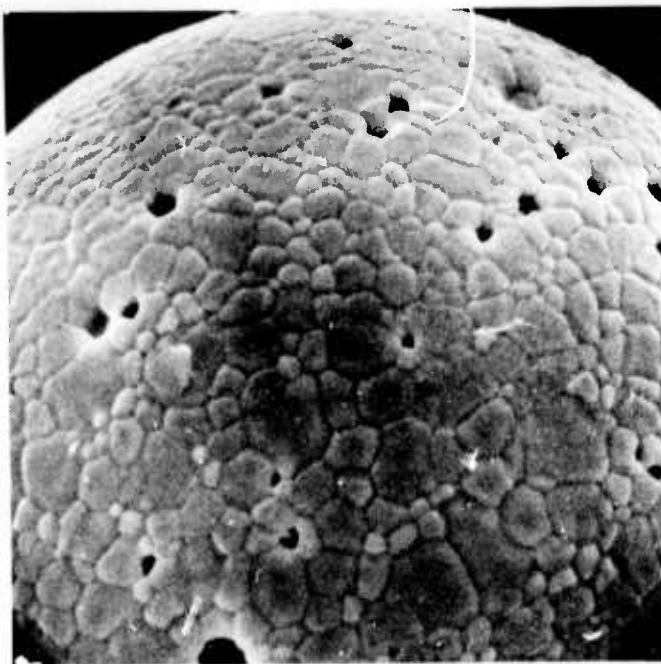


Figure 47 SEM PHOTO OF ORNL UO₂ AT 5000X

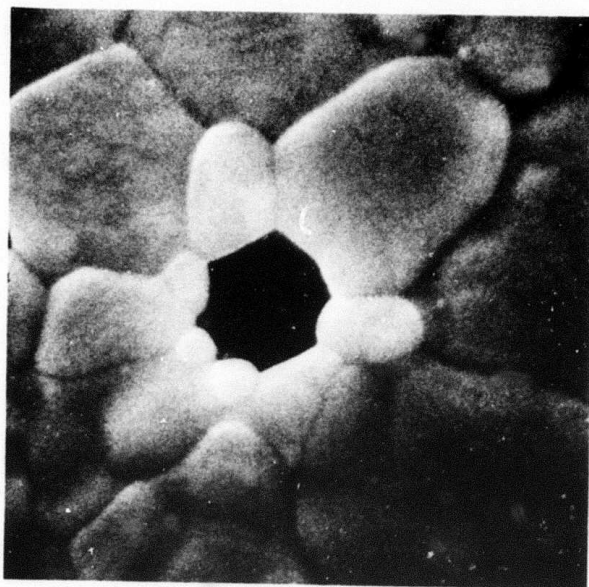


Figure 48 SEM PHOTO OF ORNL UO_2 AT 20,000X

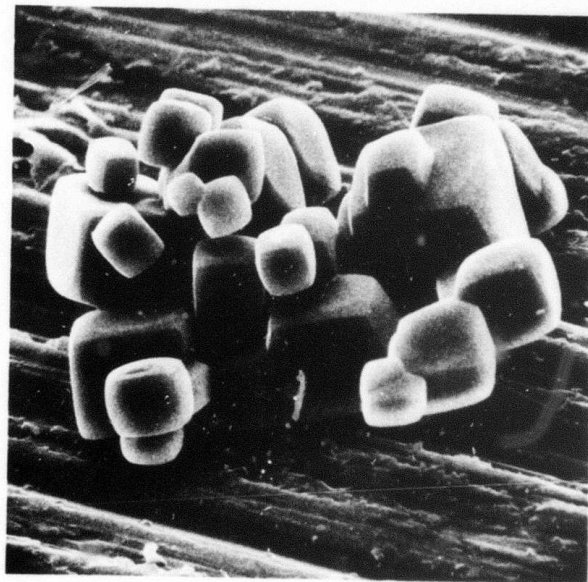


Figure 49 SEM PHOTO OF LiF AT 1,600X

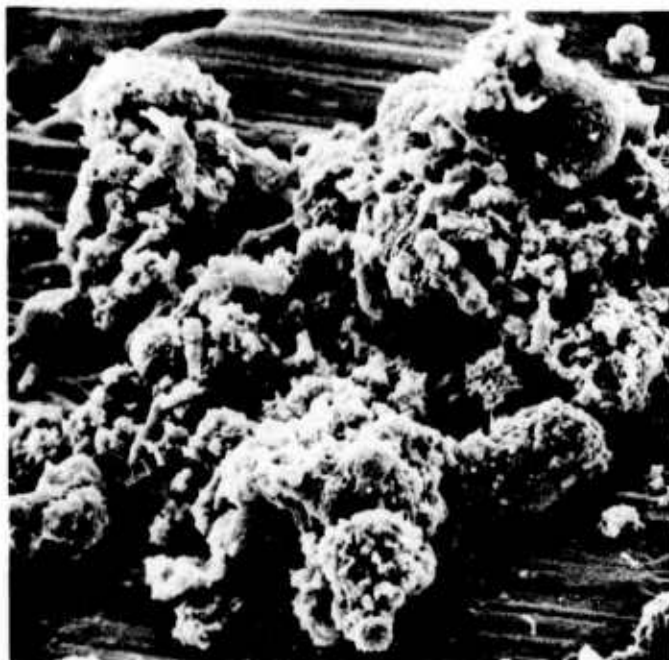


Figure 50 SEM PHOTO OF CaF_2 AT 750X

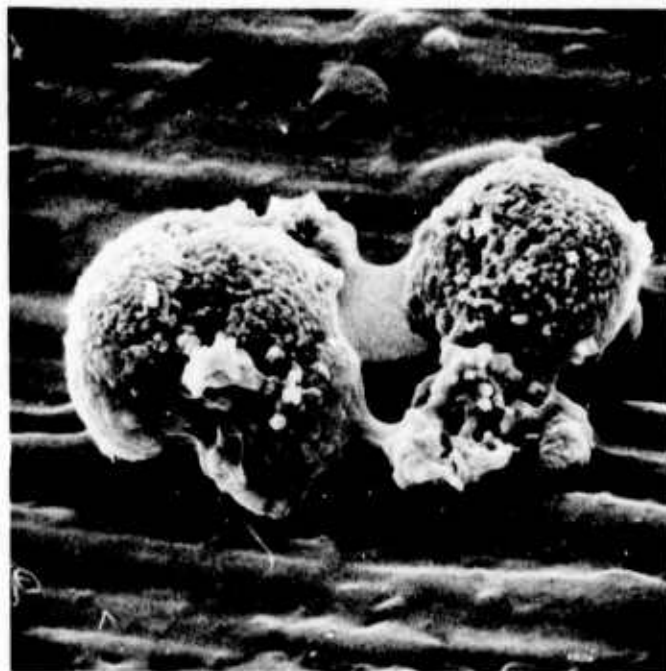


Figure 51 SEM PHOTO OF CaF_2 AT 1,500X

These materials were further characterized by applying them to air/water interfaces in their as-received condition. The results of these tests are given below.

When ThO_2 (ORNL) and ThO_2 (ALFA) were sprinkled on the water's surface, most particles sank. A very small amount of material resided on the surface as clumps of 2 to 3 particles. However, this was not a true de-agglomeration.

When CaF_2 was sprinkled on the water's surface, it exhibited some small amount of surface activity. Microscopic observation showed small bubbles attached to chains of particles on the surface.

For LiF , sinking of most of material was observed. Chains of particles formed on the water's surface from those particles which did not sink. Bubbles were observed microscopically, indicating a reaction with water.

The most interesting observations were made with UO_2 (ORNL). This material immediately flashed out with very little sinking. The result was surprising, given the large size of the particles. Within several minutes, the particulates on the surface came together into a disk. As was reported in Section 3.1, this was probably due to the ferromagnetic properties of trace quantities of iron in the sample. Attempts to measure a surface-active component on the UO_2 which was producing the spreading proved none existed. Two very sensitive techniques were used; first, the film balance of the Langmuir trough and second, the change in the contact angle of a distilled water drop on Teflon after touching the particles to the drop. The reason for the initial spreading of UO_2 (ORNL) is not known at this time.

After roof top "weathering" in containers similar to those used in Group 1 tests, the materials were re-examined for their surface activity when sprinkled on water.

In all cases, the materials behaved identically to the preweathered materials with no measurable increase in particle deagglomeration as determined by sampling the surface with prepared TEM grids.

3.5.3 Analysis of Artificially Weathered Particles

Experiments aimed at inducing controlled weathering of several particle types were carried out in Calspan's Ashford facility. This facility is described in Appendix 3.

The effects of the weathering were tested, in part, by an analysis of spread samples of these artificially weathered particles at the air/water interface. The results were compared with observations using unweathered particles of the same types.

The particles to be weathered were placed in separate Petri dishes and positioned on a raised cover within the Ashford test chamber. The location of the test specimens within the chamber is indicated by an arrow in Figure 52.

Small quantities of the following particles were placed in the chamber for weathering: (1) calibrating carbon; (2) kaolin clay; (3) UO_2 (supplied by Dr. Kaiser); (4) Alcoa AlBon #552 leafing Al powder particles passed through a 325 mesh screen; (5) glass microbeads, and (6) UO_2 (ORNL). These particles were artificially weathered for 6 days. During this time they were in the chamber where photochemical experiments were being performed. The following conditions prevailed within the chamber during this time.

Exp. No.

- | | | |
|---|--|-----------|
| 1 | particles exposed to clean filtered air for . . . | 24 hours; |
| 2 | particles exposed to high humidity for | 2 hours; |
| | 3.5 ppm NO_2 , 3.0 ppm propylene | 4 hours; |
| | light rain produced by distilled water rinsing of chamber walls; | |
| | 0.1 equivalent sunlight, and filtered air for . . | 18 hours; |

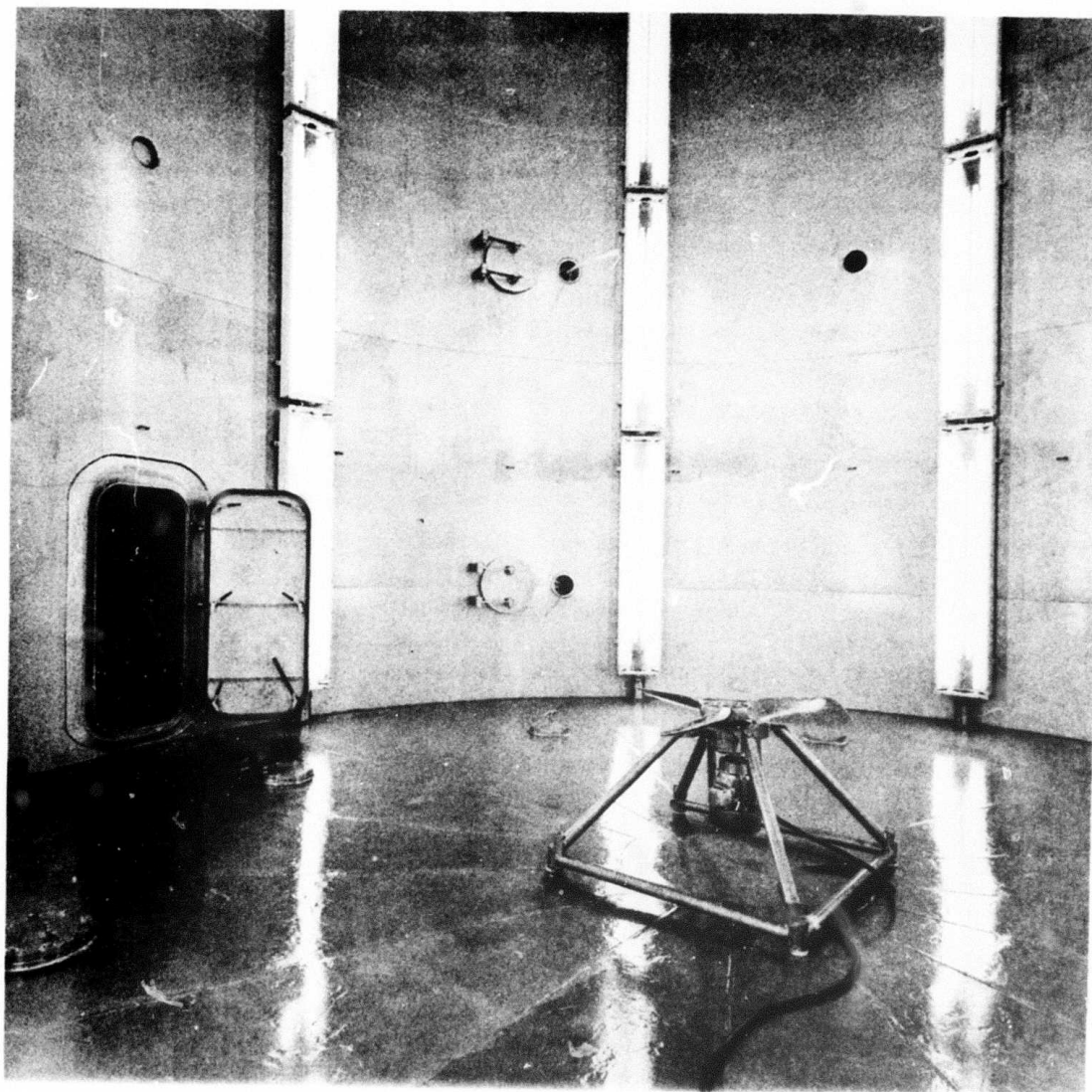


Figure 52 INSIDE VIEW OF CALSPAN'S 600 m³ PHOTOCHEMICAL AEROSOL CHAMBER

Exp. No.

3	particles exposed to clean filtered air	24 hours;
4	particles exposed to high humidity for	2 hours;
	0.75 ppm SO ₂ &NaCl nuclei (very small amount). . .	4 hours;
	0.1 equivalent sunlight, and filtered air for . . .	18 hours;
5	particles exposed to clean filtered air for . . .	24 hours;
6	particles exposed to high humidity for	2 hours;
	3.7 ppm NO ₂ , 3.0 ppm propylene, NaCl nuclei . . .	4 hours;
	0.1 equivalent sunlight, filtered air for	24 hours.

During the exposure to artificial sunlight, pollutant gasses were introduced. Also, fog and drizzle were present during the high humidity conditions.

The actual exposure received by the particles would be improved if they were mechanically aerosolized into the chamber. These experiments were of value, however, because they revealed whether nonairborne exposure would affect separability of the particles (when spread at the air/water interface, for instance). Such weathering did occasionally produce enhanced bulk particle spreading, but no data are presented here since actual enhanced submicron particle separation was low and has not been statistically established.

Experiments which remain for follow-on work would assess the weathering of similar particles which were made airborne under the same weathering conditions. Assessments of weathering effects would be determined from particle separations produced at the air/water interface or from colloidal suspensions in chloroform. An extension to "weathering" of particulates would be to treat the material as nuclei which would serve as condensation nuclei in fog formation as is discussed in Section 3.6.

3.6 SEPARATION BY NUCLEATION

Essential in the scheme of separation by nucleation would be the dissemination of the material of interest as individual particulates. Some

concept of this process is depicted in the following Figure 53. In this scheme, a particle classifier would be used to collect the submicron particles previously separated by ultrasonification in one of the wetting liquids, already proven useful.

3.6.1 Particle Isolation and Marking Within Snowflake Replicas

Under separate funding, a project team member has developed a method whereby ice crystals are nucleated on small particles injected into an aerosol chamber. Conceptually, this scheme could be applied to environmental particulates also introduced into the test chamber, as depicted in Figure 53. These ice crystals (snowflakes) are easily collected on sample slides, replicated (i.e., coated) with a permanent plastic film, and the water allowed to sublime away.

Such studies have been completed in a preliminary fashion. Replicated snowflakes, examined in both light and electron optical systems, show the original small nucleating particles within each unique snowflake replica. Thus, if particles can first be separated in a gaseous medium, it appears that the separation could be maintained by promoting condensation on the particles and freezing prior to collection and replication. The crystal replicas could then serve as permanent and unique "addresses" for separated particles when transferred from instrument to instrument.

Figure 54 shows some typical particle-containing snowflake replicas.

Resources of our current program were too limited to allow the properly detailed experiments to be initiated. Follow-on effort should consider the nucleation techniques of particle separation and "addressing" more deliberately.

3.7 OTHER TECHNIQUES TO PRODUCE PARTICLE DEAGGLOMERATION

In the course of this program, two new schemes to produce particle separations were initiated. One of these simply involved replacing the subphase

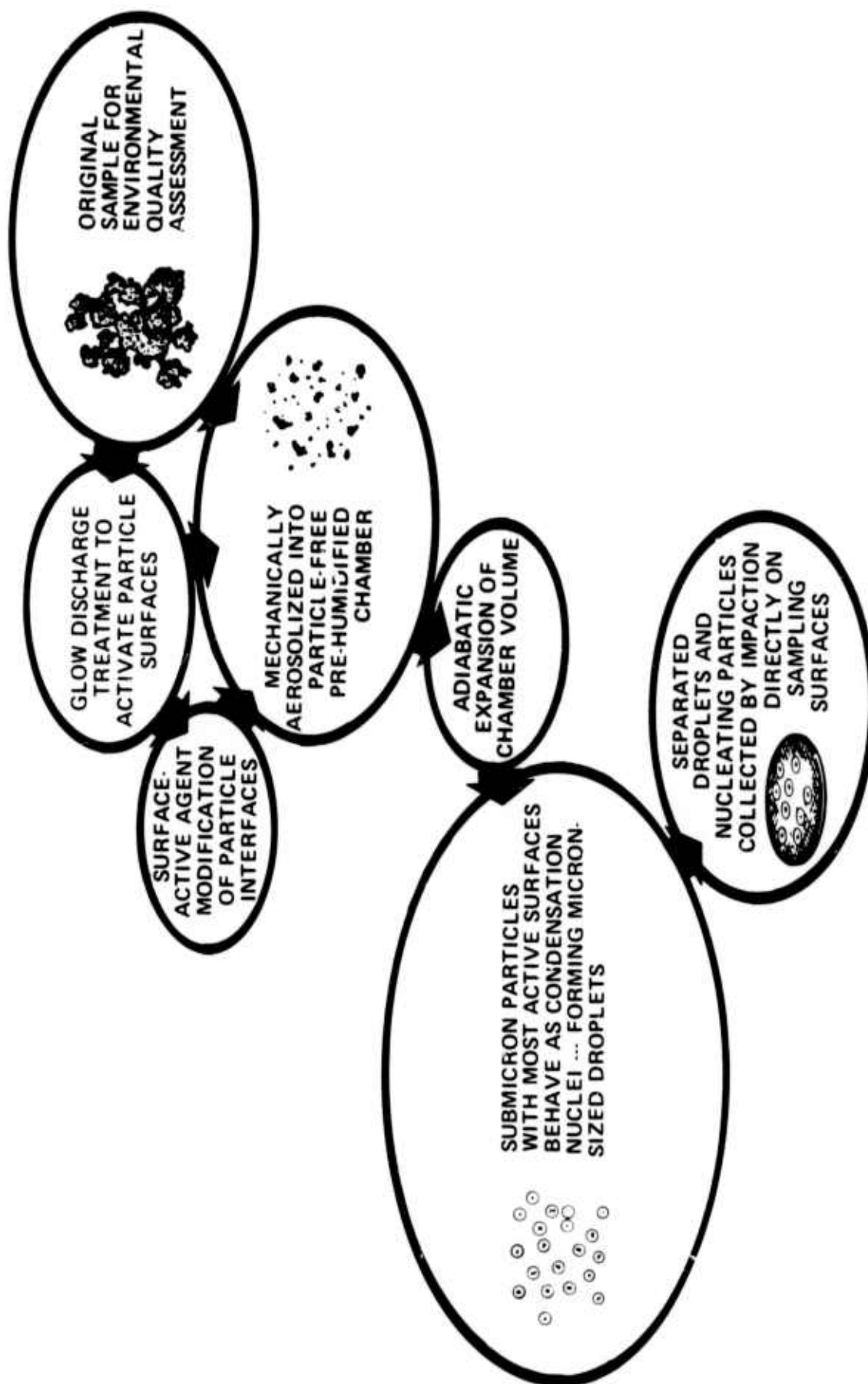


Figure 53 SEPARATION BY NUCLEATION

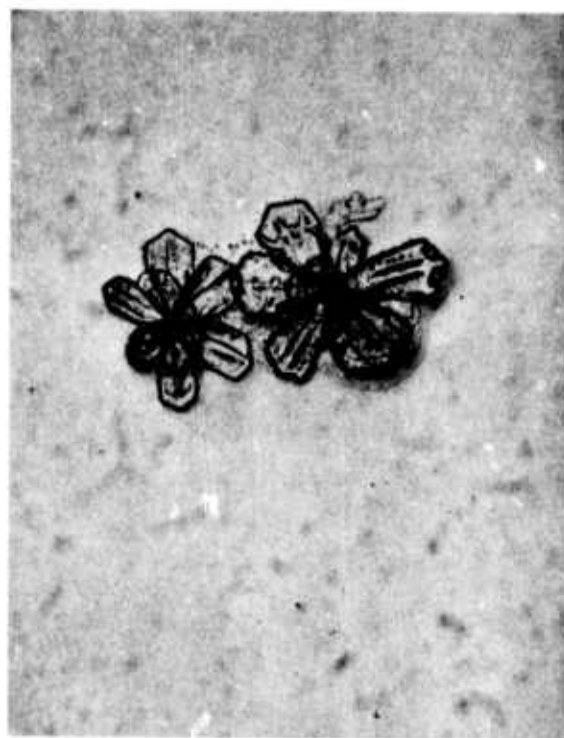


Figure 54 ICE CRYSTAL REPLICAS AND PARTICLES LOCATED WITHIN THEM

liquid in the spreading experiments by higher density liquids in order to overcome particle sinkage problems. For example, a mercury subphase was tried when working with ORNL-UO₂. UO₂ (with added poly-benzyl glutamate) in chloroform was spread on a cleaned mercury surface.

Although good visual spreading was observed on mercury, it was extremely difficult to sample the particles without accepting some mercury contamination. Polyethylene sheets, placed over the particles on a mercury surface and then gently peeled back, were most useful in recovering most of the particles for examination in the optical microscope. Examination of these particles revealed many microglobules of mercury and/or mercury contaminated particles. It was concluded from this work that the utility of a mercury subphase was defeated by its gross contamination or modification of the particles. The potential utility of other dense, but nonmetallic liquids warrants further study.

Bubbling air through a particle-bearing solution in the process of being ultrasonically treated was another technique studied. This technique was devised in order to circumvent the reagglomeration of particles resulting when a drop of liquid containing particles is allowed to dry on a prepared grid. In this method, particles adsorbed to the surface of breaking bubbles were captured for examination in our transmission electron microscope. This technique used ultrasonification as a preliminary means of breaking down the agglomerated particles and a dispersing aid to maintain the dispersion of particles in the liquid. Transmission electron microscope grids were used to capture the particles released by bubbling air through the liquid-particle mixture.

Examination of the TEM grids exposed to the breaking bubbles revealed numerous individual particles. From the grids examined, there appeared to be a preference for collection of the smaller particles within the original sample. The number of particles captured after a 2 minute exposure was extremely low, (e.g., 3 particles in 60 sq. microns), unfortunately.

In order to increase the number of particles captured, longer sampling times could be used. Another approach was to apply a film of collodion on the water surface prior to bubbling. When bubbling started, bubbles escaped only around the film edges. In this manner, a large number of particles were captured; however, the particles were present as multi-dimensional arrays, stacked many particles high. Figures 55 and 56 are typical regions of particles produced by this technique. On occasion areas such as those in Figure 57 were seen.

The technique works best with a very thin polymeric film on the surface of the liquid. Also, the number of particles collected appears to be controllable by the dispersion aid, air pressure, ultrasonic energy and sampling time. This technique deserves further study.

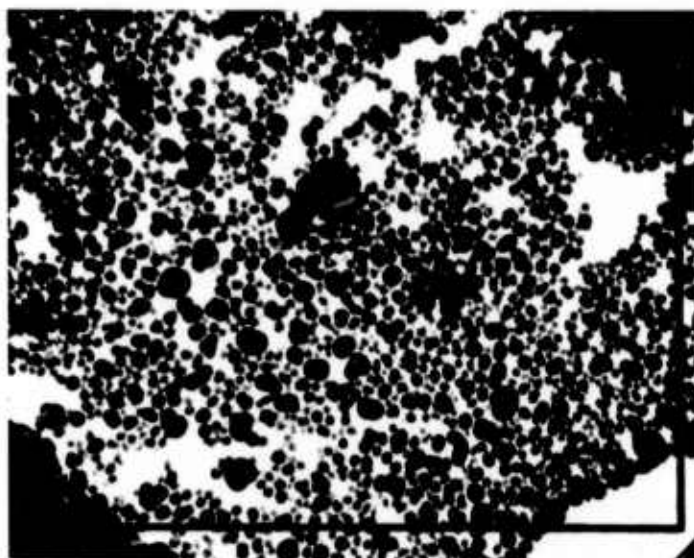


Figure 55 CARBON SPHERES BUBBLED INTO PLASTIC FILM

— 1 μ m

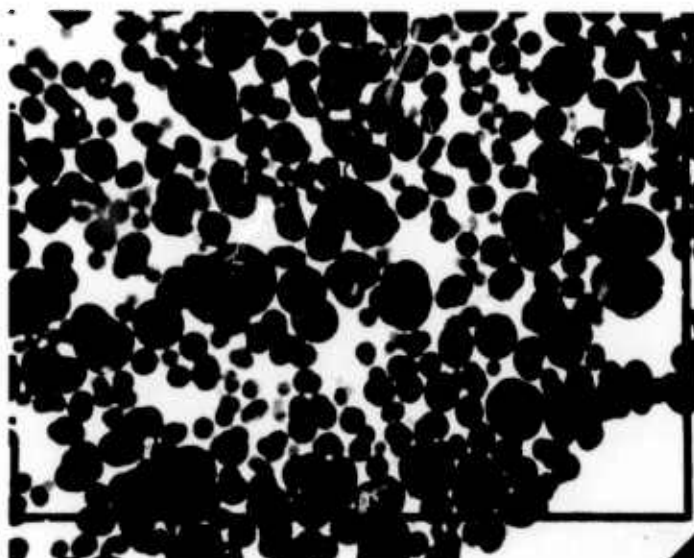


Figure 56 CARBON SPHERES BUBBLED INTO PLASTIC FILM

— 1 μ m

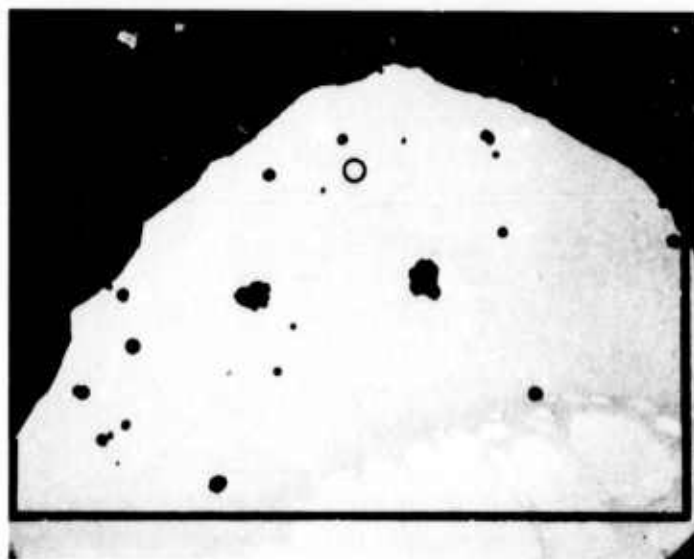


Figure 57 CARBON SPHERES BUBBLED INTO PLASTIC FILM — FEW AREAS NOTED WITH THIS TYPE DISTRIBUTION

— 1 μ m

Section 4

CONCLUSION

In this investigation of the separation of agglomerated materials using surface-active agents and surface chemical/physical techniques, a method to routinely array the separated particulates in a plane was developed. Surface chemical forces alone could not be properly utilized to accomplish the desired deagglomeration of materials. A two-step approach was found necessary in which the material is first ultrasonically dispersed in a series of wetting liquids and then drops of these liquids introduced to the air/water interface. Once spread at the air/water interface, the spread particulates are fixed by the adsorption, or preliminary addition, of a film-forming material introduced with or below the particles. Particle separations achieved by this technique are not perfect in that, in a given particle field, greater than 50% of the particles will still be in contact with their neighbors, although usually in planar array. Also, in some areas on each grid, large clumps of agglomerated/conglomerated particles are apparent, having resisted all separation forces applied. Experiments have been carried out to further separate such particle agglomerates while so displayed on a surface (e.g., on a prepared TEM grid) by surface chemical forces set up between the particles. These experiments have not been successful in that no significant additional particle separation was induced. Since this in situ particle deagglomeration was not possible, a decision must be made as to what should be done with material once displayed on a surface for viewing if it still contains agglomerates. The perfect particle deagglomeration scheme in which all materials of all types are separated from one another seems inordinately difficult to achieve when dealing with submicron particles.

The main conclusion arrived at in this work is that ultrasonic dispersion of agglomerated materials in selected liquids produces good initial particle dispersions and these separated particles can be permanently arrayed in a plane by surface chemical techniques. Reagglomeration of some of the separated particles usually takes place when they are sampled and new secondary techniques to prevent reagglomeration are required.

Section 5

RECOMMENDATIONS FOR FUTURE WORK

Several areas of new and continued research are recommended to achieve more efficient particle deagglomerations. As it does not appear likely that in situ particle deagglomerations will be possible, it will be necessary to bring about all particle separations prior to placing the material on a substrate for examination. The current standard of excellence is to produce particle deagglomerations in a volume phase by ultrasonic dispersion of the materials in suitable wetting liquids. Once this dispersion is produced, then the technique summarized in Section 3.1.7 of this report can be used to display the particles on prepared TEM grids, on surfaces for SEM analysis, or on continuous strips of film or foil.

In a follow-on program, the techniques developed in this work would be combined, so that mixtures of as-manufactured particles or environmental materials would be deagglomerated and then grouped according to type.

The colloidal suspension work presented in Section 3.2 seems especially promising for accomplishing this task. By placing the natural mixtures of materials in a series of liquids of different hydrophile-lipophile balance, it should be possible to separate the numerous particles of different types from each other. The colloidal suspensions would then be secondarily treated by interfacial stressing to achieve a planar array of particles which would be fixed in position by a support film, and then retrieved for analysis.

Another area of research recommended for further study is particle collection and fractionation by bubble processes. The deagglomeration of particles is enhanced during bubble breaking since it supplies additional energy to the particles already separated in the volume phase. It is somewhat similar to the additional separation observed when particles are retrieved from an air/water interface. Capturing the particles released from rising, collapsing, and breaking bubbles is the area requiring additional research.

Although the technique of using the particles as nuclei for snowflake or fog droplet formation was briefly discussed in Section 3.6, it should be realized that this is also a new area of research. Its probability of rapid success is low, and the problem remains of collecting most of the snowflakes or fog drops produced. Nevertheless, it would serve as an indication of the atmospheric processes which the submicron environmental particles experienced before they settled on some ambient collecting surface.

Phagocytosis is a new area of research recommended for study as a means of collecting and further separating particles dispersed in a volume phase. The collection scheme involves use of an active cell population (e.g., blood leucocytes) grown or arrayed in monolayer culture. Arraying the leucocytes on a plane has already met with success in chemical laboratories. One very useful secondary technique involves centrifugation of the particles in a mixture of blood elements. Centrifugation is carried out on a microscope slide which is spun at high speed. Figure 58 shows a field of view from a preparation of blood cells and calibrating carbon particles using this centrifuge. Further work defining the proper incubation of blood elements with the particles to be isolated is needed.

Figure 59 shows a preliminary result obtained by centrifuging ultrasonically dispersed carbon spheres from a dilute collodion solution.

Perfection of this technique requires improved knowledge of the roles which concentrations of particles and additives play. It is already clear that very high particle concentrations cause the particles to recontact each other, thereby destroying the deagglomeration originally achieved in the bulk phase.

The few areas for continued research outlined above seem to be the most promising ones to achieve a high efficiency of deagglomeration. Since

field samples, as well as mixtures of as-manufactured materials, are proposed as the materials to be experimentally deagglomerated, it is expected that the costs of performing such studies will be higher -- on a per sample basis -- than the work just completed with purified laboratory standards.

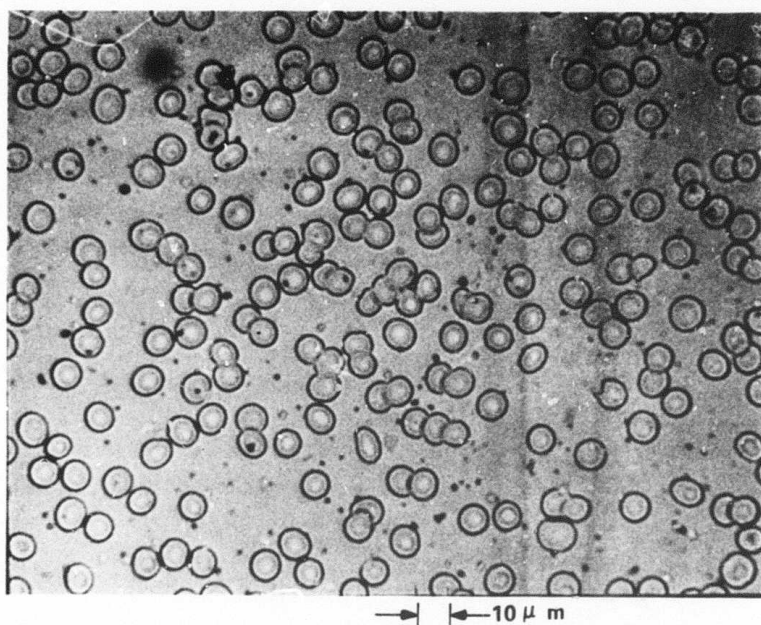


Figure 58 CALIBRATING CARBON AND BLOOD ELEMENTS CENTRIFUGED IN A PLANE

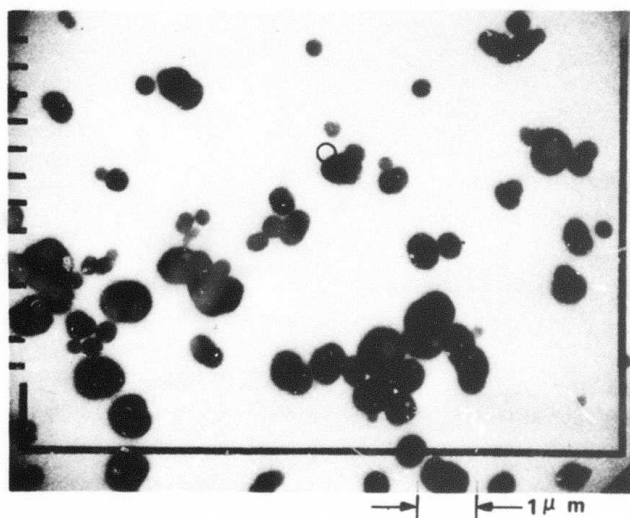


Figure 59 PREPARATION OF CALIBRATING CARBON SPHERES USING THE CENTRIFUGE TO SPIN THE SAMPLE IN A PLANE

Appendix 1

DESCRIPTION OF PARTICLES USED IN STUDYING SEPARATION TECHNIQUES:

The primary particulate materials used in studying particle separation techniques represented three different classes of materials: carbon, kaolin clay and glass microbeads. A description of these materials is given below.

Carbon - Calibrating Carbon

From Ladd Research Industries Inc., P.O. Box 901, Burlington, Vermont. The carbon particles in this material are spherical in shape with a size range of $.1\mu\text{m} \leq D \leq .6\mu\text{m}$. These particles are agglomerated in small clumps.

Kaolin Clay

From Georgia Kaolin Company, 433 North Broad Street, Elizabeth, New Jersey. The particles in this material are thin flat hexagonal plates with the longest particle dimension being smaller than $2\mu\text{m}$

Glass Microbeads

Glass beads with a diameter range of $.1\mu\text{m} \leq D \leq 5\mu\text{m}$. From Duke Standards Company, Palo Alto, California.

Other Particulate Materials Used In This Evaluation of Separation Techniques Are Described Below:

UO₂ Natural Ceramic Grade powder, Eldorado Nuclear Limited of Port Hope, Ontario, Canada. This material was supplied by Dr. R. Kaiser, AVCO Systems Division, Lowell Industrial Park, Lowell, Massachusetts, 01851. This material contains particles down to $.01\mu\text{m}$ with many large agglomerates typically of $1\mu\text{m}$ diameter.

Field samples accumulated on paper wipes outside of the Nuclear Fuel Services, Inc., West Valley, New York, and the Ashford Research Facility, Calspan Corp., Ashford, N.Y.

Erie County Air Pollution Samples

Air-borne material collected on filters in air samplers in the Buffalo Area. Samples supplied by Erie County.

Apollo 15 Moon Dust

Supplied by Dr. Cadenhead, State University of New York at Buffalo, Chemistry Department.

Carbon particles

Aqua Nuchar. Irregular particles of high surface area. From West Vaco Chemical Division, 299 Park Avenue, New York, New York 10017

Aluminum flake

ALBON #552. Nonleafing aluminum with 98% of the particles having passed through a 325 mesh sieve. From Aluminum Company of America, 15-01 Alcoa Building, Pittsburgh, Pa., 15219

The following materials were obtained from the sponsor.

ThO₂ - ALFA

Irregular fragments of cubic particles; size range $<1\mu m \leq D \leq 10\mu m$

ThO₂ - ORNL

Spheres and irregularly shaped particles. The spheres have a size range of $4\mu m \leq D \leq 18\mu m$

CaF₂ - ALFA

Rounded cubic-shaped particles with a size range of $<1\mu m \leq D \leq 5\mu m$

UO₂ - ORNL

Spheres with a diameter range of $5\mu m \leq D \leq 30\mu m$ and irregularly shaped particles

LiF - ALFA

Cubic-shaped particles with a size range $<1\mu m \leq D \leq 15\mu m$

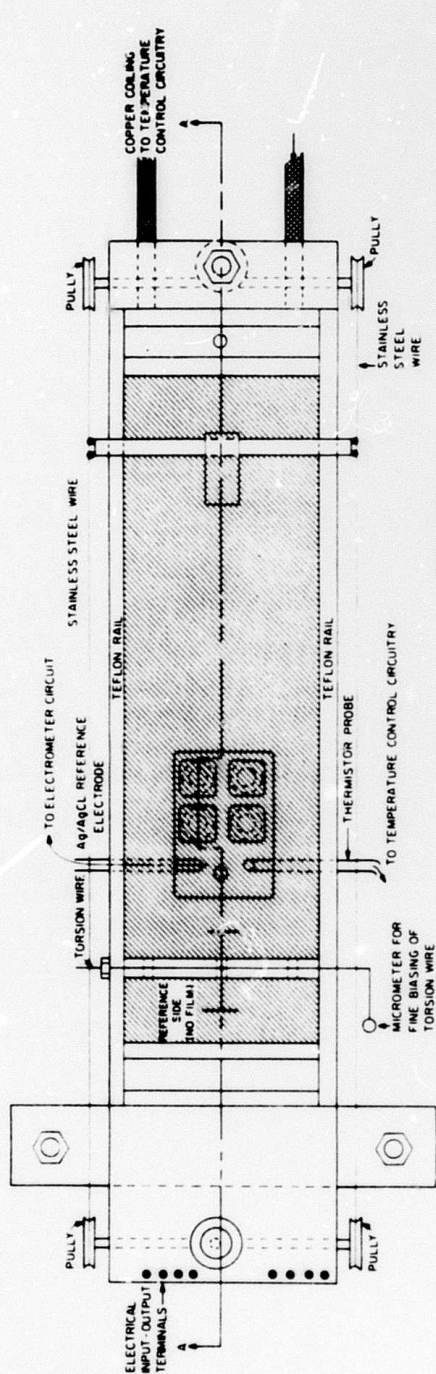
Appendix 2

AUTOMATED SURFACE BALANCE

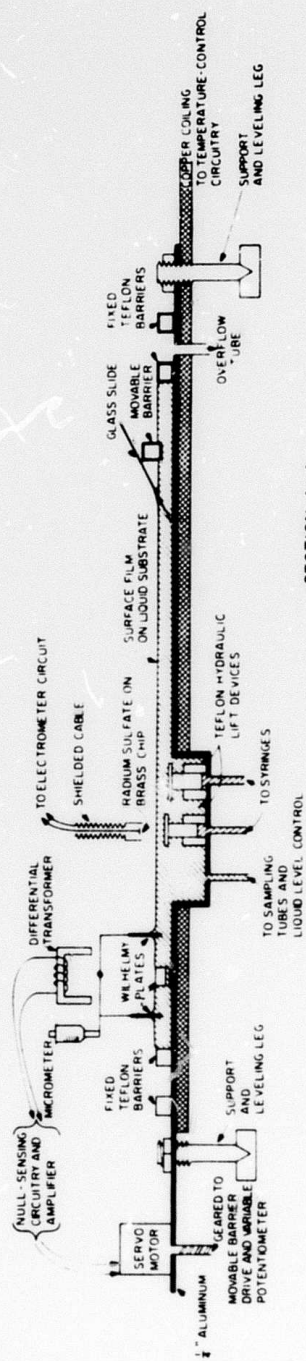
This unique and versatile research instrument is an automated, thermostatted, Langmuir-Adam teflon-lined trough with hydraulic sampling stations. It is diagramed in the Figure B-1.

This apparatus, the two-dimensional analog to a piston-and-cylinder arrangement, allows determination of basic surface-pressure-vs.-surface-area properties for interfacial films in much the same manner that pressure-vs.-volume relationships are established for gases in piston-and-cylinder devices. Use of this research instrument allows characterization of surface-active materials according to their molecular architecture. Important film parameters are also defined in this apparatus. Supporting measurements of the electrical surface potential generated by oriented interfacial films are usually made in conjunction with force-area isotherm determinations. A new dimension is added to Langmuir-Adam trough studies by the incorporation of hydraulic lift devices. These allow film samples to be taken at pressures, areas, and temperatures maintained automatically by servo circuitry. Such samples are appropriate for immediate analysis by electron microscopy, internal-reflection spectroscopy, ellipsometry and contact angle measurements.

The surface balance and associated circuitry are enclosed in a constant-environment box, and all necessary manipulations are made either remotely or through gloved openings in one face of the chamber.



TOP VIEW



SECTION A-A

Figure B-1 AUTOMATIC SURFACE BALANCE AT CALSPAN CORPORATION

Appendix 3
CALSPAN ASHFORD FACILITY

The Ashford experimental site, located 35 miles south of Buffalo, is Calspan Corporation's newest remote location for broadbased research. This 600-acre site, at which the laboratory is located, was selected for its remote location, and its wide variety of terrain features, streams and vegetative cover. This site is well-adapted to the conduct of a great variety of research and development programs, particularly those requiring a large area with limited access for reasons of safety and security, low electrical interference and non-urban terrain and atmospheric conditions.

The laboratory, with its unique aerosol chamber complex, was completed in the spring of 1966 and has been carefully designed to permit conduct of research, development and test of all classes of small munitions and ordnance, as well as fundamental and applied research in pesticide dissemination, cloud physics, fog formation and dissipation, and photochemical processes.

The laboratory consists of two main buildings which are fully separated to insure a maximum of safety and efficiency in operations. The smaller of the two buildings houses general offices and first aid facilities. The second building incorporates the following:

- a 600 m³ aerosol chamber
- a 7.5 m³ spherical recovery chamber
- chemical laboratories for instrumentation preparation, gas analyses and general analytical work
- a munition preparation room with facilities for handling and loading explosives, chemicals, cloud seeding materials, and ordnance devices

- a fully-equipped shop
- complete facilities for safe entry of personnel into the test chambers as required.

600 m³ Aerosol Chamber

The 600 m³ Ashford aerosol chamber has proven to be an extremely valuable tool for many cloud physics and air pollution studies. Although originally designed as part of an ordnance facility, extensive modifications have been made to the large chamber, making it well-suited for photochemical aerosol studies, exhaust emission tests, fog modification experiments, pesticide research, and basic problems involving aerosol physics. In the context of these investigations, relevant facility characteristics are described below.

A. FACILITY CHARACTERISTICS

(1) Physical features - The heart of the test facility is a cylindrical chamber of 10 meters in diameter and 10 meters in height. The total volume is 600 m³, making it one of the largest available test chambers in the United States, especially valuable in minimizing wall effects and closely simulating actual atmospheric conditions. The chamber wall is constructed of 0.5 inch plate steel designed for pressure differentials up to 9 psig and is coated with a specially fluorinated epoxy.

(2) Chamber surface - The chemically resistant epoxy coating used to cover the inner chamber surface was developed at the U.S. Naval Research Laboratory. This coating material is a highly fluorinated epoxy-polyurethane co-polymer. The in situ curing of the polyurethane base enables good adhesion to the underlying aluminized polyurethane surface. The very high fluorine content provides, in analogy to fluorocarbon polymers, both high chemical stability and low surface energy, while the high reflectivity enhances the effective path length of radiation used in photolysis experiments. Such favorable physical and chemical characteristics add further to the capability

of the chamber in minimizing possible wall effects during photochemical aerosol studies.

(3) Air purification - A schematic diagram of the chamber air ventilation system is shown in Figure C-1. Absolute filters are incorporated to permit virtually total removal of particulates (<200 Aitken nuclei/cm³) in the submicron range. Impregnated charcoal filter panels have been installed to enable the removal of most gaseous contaminants. The test facility is located in a rural area about 35 miles from the industrialized areas of Buffalo, New York so that most sources of man-made contamination are minimal. Some of the most difficult to remove contaminants such as CO and CH₄ are normally present in the unpurified ambient air only at minimum concentrations. The air purification system is thus capable of preconditioning the chamber for studies of preconditioning the chamber for studies of pollutant effects even at minute concentrations.

(4) Water purification - The chamber is equipped with a water flush system as shown schematically in Figure C-1b. Prepurified water (or other decontaminating agent) can be introduced into the chamber through a rotating jet sprayer. In normal operation, this flush system serves a dual function of introducing water for chamber humidity adjustment and for chamber wall surface cleaning. A specially designed water purification system (particle filters and demineralizers) is being incorporated into the water spray system in order to provide a chemically pure washdown supply.

(5) Photoirradiation sources - Photolysis lamps simulating the earth's ground level solar radiation spectrum (in the 3000 Å to 6000 Å region) have been installed around the chamber wall to permit a uniform intensity distribution of light within the chamber. Twenty-four individual light fixtures, each containing two GE-F96PG17/D daylight lamps and two GE-F72T12/HO/BL black-light lamps, are arranged in three horizontal and eight vertical rows radially spaced equally along the chamber wall. Each of the light source combinations is encased in a gastight enclosure equipped with a 15" x 96" tempered glass front panel. Forced air cooling is used to minimize possible temperature rises at these light source fixtures.

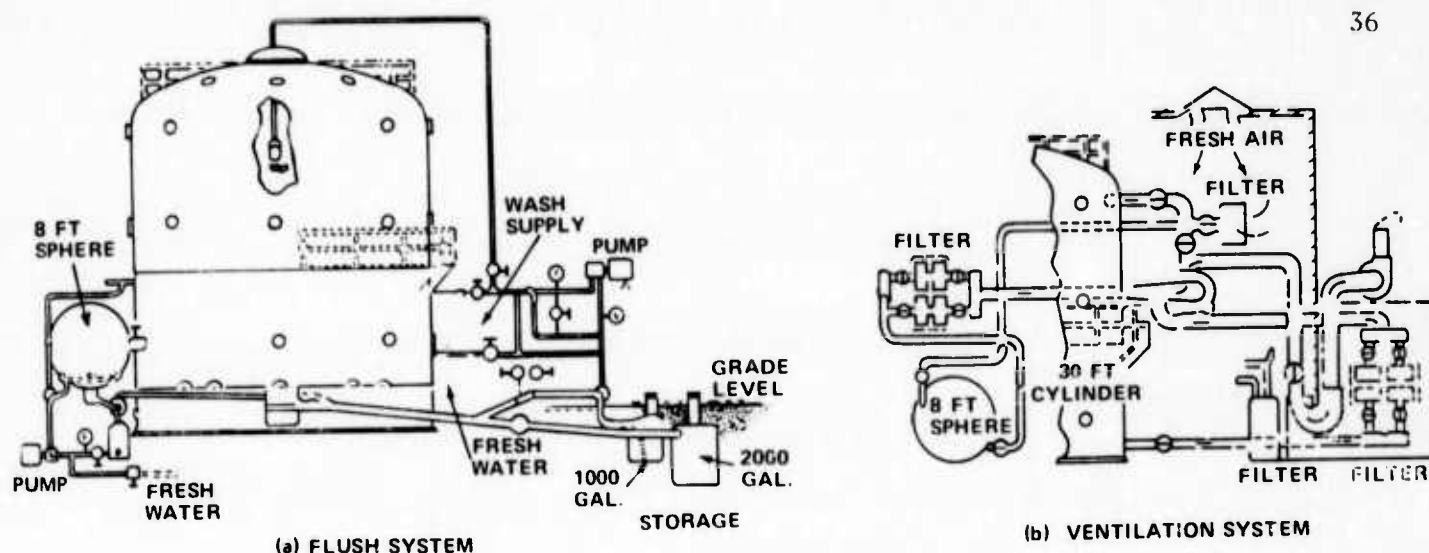
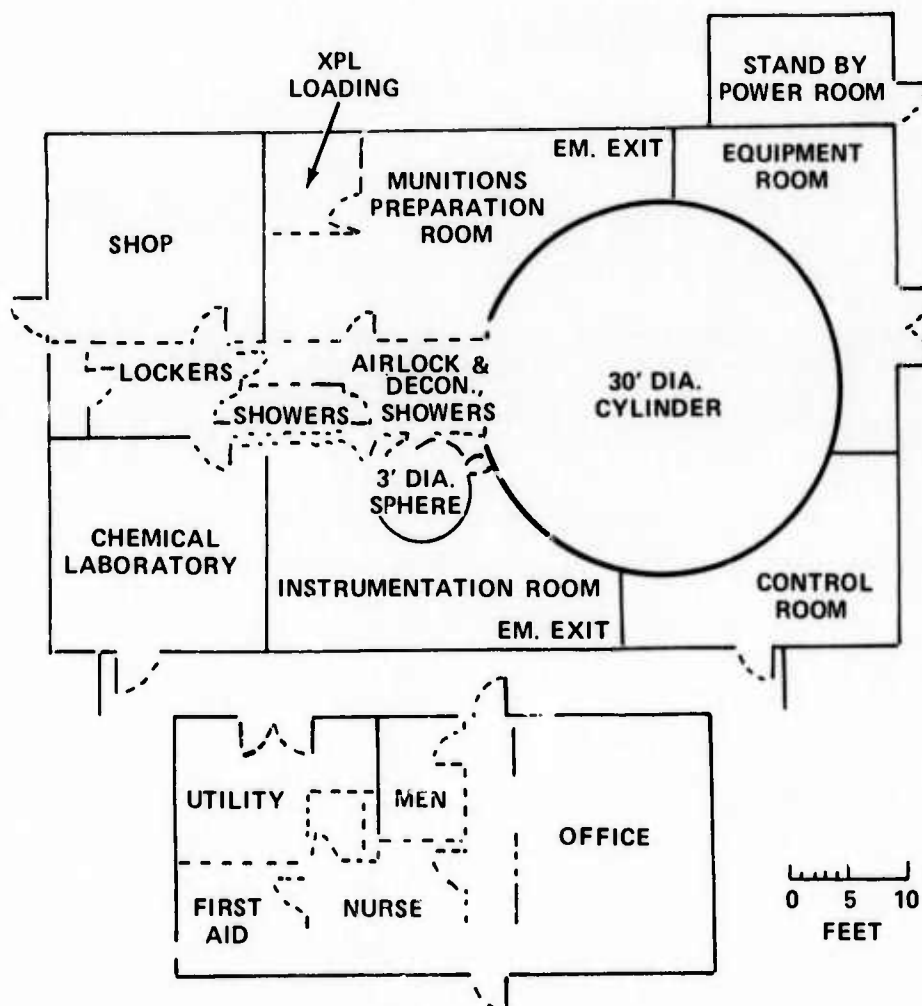


Figure C-1 CHAMBER SCHEMATIC



(6) Aerosol monitoring instrumentation - Equipment available for monitoring the various particle and liquid droplet parameters are as follows:

- (a) Two transmissometers capable of continuous recording visibility in laboratory fogs at levels of 1.2 and 4.5m, respectively. The light path length for each unit is 18 m.
- (b) A gelatin slide drop sampler, to provide samples for microscopic evaluation of droplet size spectra. Droplets with radii between $1\mu\text{m}$ and several tens of microns are routinely samples with this device.
- (c) A xenon flash illuminated sampler permitting close-up photographic recording of total drop number concentrations.
- (d) Gardner particle counters for monitoring total particulate concentration.
- (e) Three Calspan-built thermal diffusion chambers for cloud condensation nuclei concentration measurement. One of these units, the haze chamber, produces controlled relative humidity between 95 and 100%. The other two produce controlled supersaturations between 0 and 3% (i.e., 100% to 103% RH).
- (f) Plans are being made to acquire a Whitby aerosol analyzer for aerosol concentration and size distribution determinations and an integrating nephelometer for aerosol light scattering and visual range measurements.

(7) Gas analysis instrumentation - Highly sensitive instrumentation for analysis of prevalent gaseous pollutants is a part of the test facility capability.

- (a) Bendix Model 8002 ozone analyzer - An instrument based on the principle of photometric detection of chemiluminescence resulting from the reaction of ozone with ethylene.
- (b) Bendix Model 8101-B nitrogen oxides analyzer - Photometric detection based on chemiluminescent reaction between NO and ozone. NO₂ is detectable through a prior conversion to NO.
- (c) Bendix Model 8300 flame photometric sulfur analyzer - The detection principle is based on sulfur atom excitation in a hydrogen rich flame. Total sulfur, SO₂ and H₂S can be differentiated through the use of appropriate absorption filters.
- (d) Hewlett-Packard Model 5750 gas chromatograph - An instrument equipped with dual column and dual flame ionization detectors capable of analyzing either the total hydrocarbon or individual organic components. A CO to CH₄ conversion reactor is being designed to permit CO analysis with this instrument.
- (e) Spectrophotometric instruments - A number of IR, UV, and visible range spectrophotometers are available for qualitative identification of gaseous components in the chamber air samples.

7.5 m³ Sphere

The small 7.5 m³ sphere is connected to the larger aerosol chamber and can serve as either a functioning barricade (with the output of a test device being fed into the larger chamber) or a completely isolated test system. The sphere is 8 feet in diameter, constructed of 1.5 inch steel plate and is designed for working pressures of 250 psi. This sphere is primarily designed

for munitions testing and in this respect is particularly valuable when testing explosive devices which would otherwise damage the special surfaces of the large chamber.

Personnel have access to the large and small chambers through a large door and a 21-inch hatch, respectively, from a common air lock compartment.

In normal operation, test devices and instrumentation can be inserted in the chambers through strategically located glove boxes. Viewing ports are circumferentially located in the walls of the chambers to facilitate optical instrumentation as well as visual assessment of performance.

Ease of operation, adaptability to new test requirements, flexibility for instrumentation, and personnel safety were primary considerations in the design of the facility.

B. OPERATIONAL CAPABILITIES: CLOUD PHYSICS AND PHOTOCHEMICAL AEROSOL STUDIES

The Ashford facility floor plan is shown in Figure C-2. Fog seeding, aerosol formation and photochemical reaction studies are being conducted within the above-described facility.

(1) Cloud nucleation and fog formation studies - The experimental procedure normally consists of fog production and characterization, nuclei seeding, and aerosol detection steps. First, the chamber wall is wetted thoroughly with water from the rotating spray nozzle. The chamber air is pressurized to about 30 mb, and the air is circulated to establish the desired equilibrium conditions. Fog formation is induced by venting the chamber air at a controlled average rate of about 3 mb/min. After reaching ambient pressure, fog persistence is achieved by continued slow expansion of the chamber air to a pressure about 30 mb below ambient. In this way, fogs and clouds closely approximating those found in nature can be produced. Seeding concepts designed to improve visibility in fog can be tested by injecting

artificial nuclei into the fog with a jet mill located near the chamber ceiling. Nuclei and aerosol monitoring are achieved through use of the instrumentation described in the preceding section.

(2) Aerosol formation studies - Experimental programs are in progress to study atmospheric aerosol formation processes. Effects of relative humidity, particulate type and concentration, and various gaseous contaminants on aerosol formation rates are being studied. An important objective of one program is to examine the effect of automobile exhaust emissions and other atmospheric pollutants on aerosol formation and atmospheric visibility.

(3) Photolysis reaction studies - Recent chamber modifications providing high intensity illumination sources, air purification systems, and inert chamber surface coatings are designed for upgrading the facility for chemical reaction studies. Photochemical reactions are known to play important roles in gas to particle conversions. The interrelationship between aerosol size distributions, gaseous constituents, and photochemical processes will be a subject of major interest in research programs planned for utilization of the Calspan Ashford chamber facilities.